

Oxidative and Reductive Degradation of Mixed Contaminants by Bifunctional Aluminum

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Abstract: Transformation of various contaminants including carbon tetrachloride (CT), methyl *tert*-butyl ether (MTBE), trichloroethylene (TCE), and bis(2-chloroethyl) ether (BCEE) using bifunctional aluminum was examined in batch reactors. Reductive degradation was observed only in reactions with CT while MTBE, TCE, and BCEE underwent oxidative pathways. In a batch reactor containing both CT and MTBE, oxidation of MTBE and reduction of CT by bifunctional aluminum took place simultaneously in the presence of oxygen. The MTBE was degraded to *tert*-butyl formate, *tert*-butyl alcohol, acetone, methyl acetate, and isobutene while the reduction of CT produced chloroform and dichloromethane. This indicates that bifunctional aluminum has a dual functionality of decomposing both oxidatively and reductively degradable contaminants together. Aluminum metal serves as a reductant while oxygen acts as an oxidant. Oxidizing capacity of bifunctional aluminum, resulted from reductive activation of dioxygen (O₂), is dependent on both oxygen level and effectiveness of reductants. It was found that the redox potential of reaction systems can function as a simple indicator to determine the oxidizing capacity of bifunctional aluminum.

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Introduction

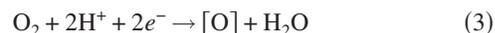
The use of zero-valent metals (e.g., iron, zinc, and aluminum) has shown much success in treatments of a wide array of contaminants (e.g., Gillham and O'Hannesin 1994; Matheson and Tratnyek 1994; Arnold and Roberts 1998; Lien and Zhang 2002a). In particular, implementation of full or pilot scale in situ permeable reactive barriers (PRBs) using zero-valent iron as a reactive media has been demonstrated to effectively remediate groundwater contaminated with chlorinated organic solvents (e.g., Puls et al. 1999; Wilkin et al. 2003). The fact that chlorinated organic solvents such as trichloroethylene (TCE), vinyl chloride, and carbon tetrachloride (CT) are readily degraded by zero-valent iron is not surprising because iron serves as an effective reductant (Matheson and Tratnyek 1994). Iron releases electrons through iron corrosion while contaminants such as CT undergo reduction reactions gaining electrons to form less chlorinated intermediates such as chloroform



While most attention was attracted by the powerful reducing

capacity of zero-valent iron, its oxidizing capacity seemed to be overlooked long ago. Recently, it has been found that zero-valent iron is capable of oxidizing benzoic acid, carbothioate herbicide, and molinate (Joo et al. 2004, 2005). The oxidizing capacity is attributed to the generation of hydroxyl radicals through the formation of hydrogen peroxide in the presence of iron and oxygen. Fenton's reaction that involves hydrogen peroxide reacting with Fe(II) may occur in the zero-valent iron system.

Bifunctional aluminum, prepared by sulfating zero-valent aluminum with sulfuric acid, has been shown to oxidatively degrade fuel oxygenates such as methyl *tert*-butyl ether (MTBE) in the presence of oxygen (Lien and Wilkin 2002; Lien and Zhang 2002b). Sulfation of aluminum resulted in the formation of catalytic sulfur-containing species at the surface. Oxidizing capacity of bifunctional aluminum was attributed to the reductive activation of dioxygen (O₂). The reductive activation of dioxygen is a process that catalytically converts oxygen into reactive radical oxygen species in the presence of electron donors such as NaBH₄, reduced nicotinamide adenine dinucleotide phosphate (NADPH), and zinc (Otsuka et al. 1990; Sheldon 1994; Akita and Moro-oka 1998). The formation of radical oxygen species can generally be expressed as the following equation where [O] represents a reactive reduced oxygen species (Akita and Moro-oka 1998):



The reduced oxygen species are strongly electrophilic and therefore can serve as strong oxidants for oxidative reactions. On the other hand, electron donors creating reducing conditions facilitate reductive reactions. In other words, Eq. (3) pointed out a possibility for zero-valent metals to simultaneously support oxidative and reductive degradation of contaminants. Therefore, it is possible to engineer a system where gasoline oxygenates can be oxidized through the reductive activation of dioxygen, while chlori-

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nated organic solvents can be reduced by taking advantage of reducing conditions.

This work, a proof-of-concept study, was aimed at providing fundamental understanding and evidence of how bifunctional aluminum can simultaneously degrade oxidized and reduced contaminants in the same reaction system. Methyl *tert*-butyl ether and CT were chosen as major model compounds in reactions with bifunctional aluminum in the presence of oxygen. Carbon tetrachloride with a saturated carbon oxidation state of +4 was used as a probe for reductive reactions and MTBE was used as a probe for oxidative reactions. Chlorinated organic solvents and gasoline oxygenates are two common classes of synthetic organic compounds that are often detected in contaminated groundwater (Squillace et al. 1999; Johnson et al. 2000). In addition, contaminants including TCE and bis(2-chloroethyl) ether (BCEE) were also tested. The TCE has been known to undergo both oxidative degradation (e.g., Fenton's reaction) (Glaze et al. 1993; Pignatello et al. 1999) and reductive degradation (e.g., zero-valent iron reduction) (Arnold and Roberts 2000). Bis(2-chloroethyl) ether is part of the large class of chloroalkyl ethers used as solvents in several industrial processes and as an intermediate in the manufacture of chemicals (WHO 1998). Elevated concentrations of BCEE (200 ppm) have been found in contaminated groundwater in Southeast Texas, caused by the leachate from a landfill (Huang et al. 1999).

The results from batch experiments on the rate and extent of contaminant degradation, and the identification of reaction products are presented. Analysis of product distributions and reaction rates provides insight into degradation processes, and the effect of environmental factors on degradation rates. In addition, insights gained from this study offer a better understanding of potential applications and limitations of this novel material for further research.

Materials and Methods

Materials

Methyl *tert*-butyl ether (MTBE), *tert*-butyl formate (TBF), *tert*-butyl alcohol (TBA), methyl acetate (MA), isobutene, acetone, CT, chloroform (CF), dichloromethane (DCM), TCE, and BCEE with reagent grade or better (>99%) were purchased from Aldrich. The materials 1.0 N H₂SO₄ and concentrated HCl were obtained from Fisher and EM Science, respectively. Aluminum powder (+99%, ~20 μm) was purchased from Aldrich.

Preparation of Bifunctional Aluminum

Bifunctional aluminum was prepared in a fume hood under ambient temperature and pressure. Ten milliliters of concentrated HCl were slowly added to a 500 mL glass beaker containing 5.0 g of aluminum powder and the suspension was mixed with a magnetic stirrer. Immediate fume evolution was observed. Ten milliliters of distilled water were added quickly to dissipate heat for 30 s. A 0.5 mL of 1.0 N H₂SO₄ was added into the suspension and it was mixed again for 30 s. Five milliliters of concentrated HCl were added in the suspension followed by the addition of 1.0 mL of 1.0 N H₂SO₄. After the suspension was stirred for 30 s, 5 mL of concentrated HCl was added again and then the suspension was quenched with 15 mL of distilled water. Finally, the suspension was stirred for 20 min before bifunctional aluminum was harvested via vacuum filtration.

Batch Experiments

Batch experiments were carried out in 150 mL serum bottles containing about 1.0 g of bifunctional aluminum. For each batch bottle, a predetermined volume of stock solutions of organics was spiked into a 50 mL aqueous solution to achieve a desired initial concentration. Typical concentrations were 0.4 mM (35.2 mg/L) for MTBE, 0.33 mM (50.8 mg/L) for CT, 0.23 mM (30 mg/L) for TCE, and 0.21 mM (30 mg/L) for BCEE. Batch bottles were mixed on a wrist-action shaker (100 oscillations/min) at room temperature (22±1°C). All experiments were associated with the control tests where identical experimental conditions and initial concentration of reactants were employed in the absence of bifunctional aluminum. Analyses of organic mass in the controls indicated that the mass varied by less than 5% over the course of a typical experiment. Experiments were conducted under acidic conditions (initial pH of 3.5–4.0).

Methods of Analyses

At selected time intervals, 1 mL of aqueous aliquot withdrawn by a gas-tight syringe was diluted with 4 mL of distilled water for gas chromatography/mass spectrometer (GC/MS) analysis. A Shimadzu QP5000 GC/MS coupled to a Tekmar 3000 purge and trap concentrator was used for qualitative identification and quantitative analysis of MTBE, CT, and their reaction products. A VOCARB 3000 trap column (Supelco) was installed in the purge and trap concentrator to remove excessive water. A DB-624 column (J&W, 0.25 mm×30 m) was equipped with GC/MS. The oven temperature was programmed as follows: hold at 50°C for 5 min and ramp at 5°C/min to 100°C. Injection and detector temperatures were set at 150 and 230°C, respectively. A quadrupole mass spectrometer was set to scan from 20 to 150 *m/z* with data collection every 0.1 s. Identification of reaction products was conducted by matching the resultant mass spectral patterns with those in the National Testing and Information Service Spectral Library and further verified with the standard chemicals purchased from Aldrich.

Kinetic Analysis

Reaction rates of contaminant degradation were determined with a pseudo-first-order equation

$$\frac{dC}{dt} = -k_a C \quad (4)$$

where *C*=concentration of contaminants in the aqueous phase (mg/L); *k_a*=observed first-order rate constant (h⁻¹); and *t*=time (h). Plots of the natural logarithm of contaminant concentration versus time through linear regression analysis gave straight-line results. Observed first-order rate constants then can be calculated by linear regression analyses.

Results and Discussion

Transformation of Contaminants: Carbon Tetrachloride, Methyl *Tert*-Butyl Ether, Trichloroethylene, and Bis(2-Chloroethyl) Ether

The results for the transformation of CT by bifunctional aluminum are shown in Fig. 1. Rapid and complete degradation of CT was observed within a few hours. Chloroform (CF) and dichlo-

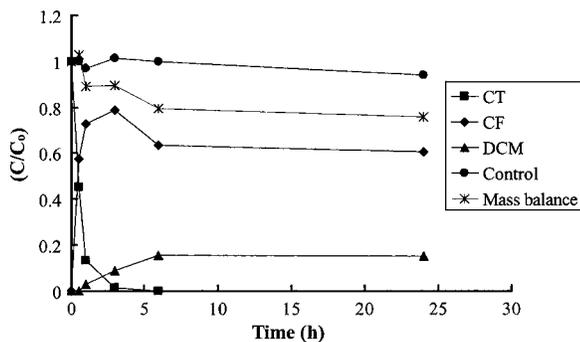


Fig. 1. Transformation of carbon tetrachloride by bifunctional aluminum

romethane (DCM) accounting for about 60.6 and 15.2% of the CT lost, respectively, were primary products. Methane was found in minor amounts (<1%). The carbon mass balance was about 75.8% at the end of the experiment. The observed rate constant of CT degradation was determined to be about 1.4 h^{-1} .

Oxidative transformation of MTBE by bifunctional aluminum has previously been reported (Lien and Wilkin 2002; Lien and Zhang 2002b). In this study, experiments were carried out under similar conditions. Results of repeated experiments were consistent with those in previous reports. Reaction products included TBF (11%), TBA (15%), MA (13%), acetone (30%), and isobutene (trace). It should be noted that there was 1 order of magnitude difference in reaction rates of MTBE degradation between two previous reports. This is because the experiments were conducted under different mixing conditions. The use of an orbital shaker providing only mild horizontal mixing conditions resulted in a lower rate constant (0.1 h^{-1}) (Lien and Wilkin 2002), whereas a wrist-action shaker mimicking side-to-side action of hand mixing led to a higher rate constant (1.0 h^{-1}) (Lien and Zhang 2002b). From the viewpoint of PRB applications, the mild horizontal mixing alone is much more appropriate than the wrist-action mixing to simulate the flow conditions of groundwater. This is because groundwater primarily moves in horizontal or lateral directions and flow rates are usually quite slow (1–500 m/year in general) (Bouwer 1978). Nevertheless, this difference did not alter conclusions as it, in fact, reflected the importance of mass transfer effect. In this study, a wrist-action shaker was used and the rate constant was determined to be approximately 1.0 h^{-1} , which is in good agreement with the previous study (Lien and Zhang 2002b).

Reaction of TCE with bifunctional aluminum was tested in the presence of oxygen. The TCE was rapidly degraded within a period of 6 h and surprisingly there were no by-products observed. Reductive degradation of TCE by zero-valent iron led to the formation of less chlorinated ethylenes and hydrocarbons [e.g., ethane in Eq. (5)] (Arnold and Roberts 2000) while oxidative degradation of TCE through Fenton's reaction resulted in the formation of chlorinated organic acids [e.g., dichloroacetic acid in Eq. (6)] (Glaze et al. 1993; Pignatello et al. 1999)

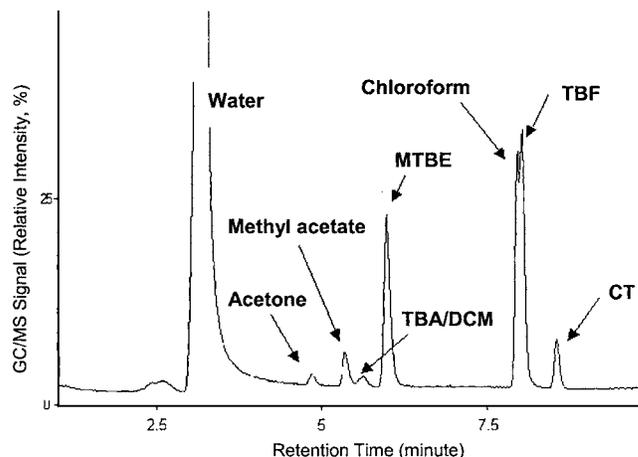
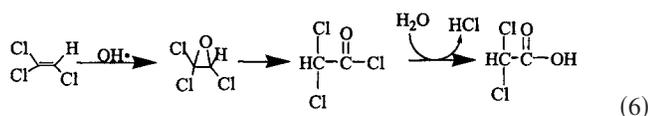


Fig. 2. Gas chromatography/mass spectrometer chromatogram measured from the transformation of a mixture of methyl *tert*-butyl ether and carbon tetrachloride by bifunctional aluminum at 1 h

Accordingly, it is likely that TCE underwent oxidative pathways to form chlorinated organic acids that are unable to be detected under the experimental conditions using GC analysis in this study. Because half-reaction reduction potential of CT to CF (0.77 V) was greater than that of TCE to dichloroethylenes (0.5–0.54 V) (Vogel et al. 1987), CT should be more favorable than TCE to undergo reductive reactions. Oxidative rather than reductive degradation occurring in reactions of bifunctional aluminum with TCE suggests that bifunctional aluminum may be capable of oxidizing certain chlorinated organic compounds such as dichloromethane and dichloroethanes that were not degraded via metal-mediated reduction (Matheson and Tratnyek 1994; Lien and Zhang 2005).

Oxidative degradation of BCEE using UV peroxidation has been evaluated (Li et al. 1995). In the presence of hydrogen peroxide, BCEE was reduced to undetectable levels after 30 min of UV irradiation and produced intermediates including 2-chloroethyl 1-hydroxyethenyl ether and 2-chloroethyl acetate. In the presence of oxygen, bifunctional aluminum effectively transformed BCEE to 2-chloroethyl 1-hydroxyethenyl ether and 2-chloroethyl acetate within 1 h. The formation of 2-chloroethyl 1-hydroxyethenyl ether was determined by GC/MS spectrum. Its *m/z* values are 15 (13%), 31 (100%), 43 (9%), and 62 (23%) where *m/z* 31 is the base peak. This is consistent with results reported by Li et al. (1995) and indicates BCEE underwent an oxidative reaction pathway.

Simultaneous Degradation of Both Methyl *tert*-Butyl Ether and Carbon Tetrachloride

Fig. 2 illustrates a GC/MS chromatogram indicating the simultaneous degradation of both MTBE and CT occurred in the presence of bifunctional aluminum and oxygen. In this study, reactions of a mixture of MTBE (0.4 mM) and CT (0.33 mM) with bifunctional aluminum were performed in the same batch system. *tert*-Butyl formate, TBA, methyl acetate (MA), and acetone were found from the MTBE degradation while the degradation of CT led to the formation of CF and DCM. Product distributions and reaction rates were similar to those observed from the single compound tested under identical conditions as mentioned above (e.g., Fig. 1). This indicates that the oxidation of MTBE and the reduction of CT can simultaneously proceed in the presence of bifunc-

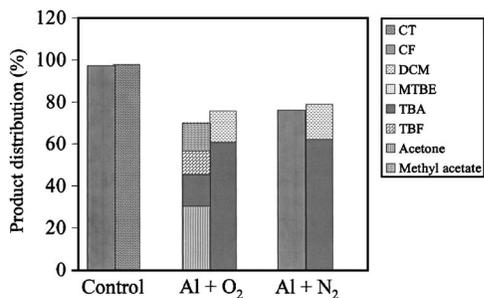


Fig. 3. Comparison of oxygen effects on degradation of methyl *tert*-butyl ether and carbon tetrachloride together (Al represents bifunctional aluminum)

tional aluminum. It should be pointed out that a very close retention time for the appearance of DCM and TBA was observed in GC analysis (Fig. 2). Both appeared at about 5.8 min. The TBA peak appeared initially but it was gradually overwhelmed by the DCM peak as the production of DCM increased in the mixed solvent system.

Impact of Environmental Factors: Oxygen and Redox Potential

Transformation of both CT and MTBE together was further conducted in the presence and absence of oxygen to compare the oxygen effect on different types of contaminant degradation (Fig. 3). To create an oxygen-free condition, batch reactors were purged with pure nitrogen for 2 h to remove dissolved oxygen before MTBE was added while experiments were carried out under ambient conditions for the oxygen-present study. As shown in Fig. 3, reduction of CT by bifunctional aluminum proceeded under both oxygen-free and oxygen-present conditions. Similar amounts of CF (~61%) and DCM (~15%) were observed in both systems. Because the aluminum is the only electron donor in the system, the reduction of CT occurring under both conditions indicates that the role of aluminum metal is the reductant.

However, degradation of MTBE with bifunctional aluminum took place only in the presence of oxygen (Fig. 3, Al+O₂). In the absence of oxygen, no reaction of MTBE with bifunctional aluminum was observed and no reaction by-products were detected (Fig. 3, Al+N₂). This indicated that bifunctional aluminum alone did not degrade MTBE. The oxygen-dependent reaction indicates that oxygen serves as a primary oxidant. Due to the basic character of etheric oxygen on MTBE, bifunctional aluminum with acidic surface should adsorb MTBE to a certain degree, which reflected to be about 25% of the MTBE lost in the absence of oxygen. Nevertheless, when the batch bottle was purged with pure oxygen gas (99.9%) in the headspace for 1 min after a contact period of 8 h, the degradation of MTBE resumed (Fig. 4). Approximately 5% of MTBE escaping from the batch bottle during the process of oxygen addition was determined. The loss of MTBE is insignificant and should largely be attributed to the high water solubility of MTBE. The transformation of MTBE to TBF, TBA, MA, and acetone was observed after the oxygen addition (Fig. 4). Although attempts were not made to measure the residual dissolved oxygen in solutions after nitrogen purging, it is clear that the purge of nitrogen should effectively lower the dissolved oxygen to a trace level where bifunctional aluminum was unable to oxidize MTBE according to the result shown in Fig. 4.

Oxidation reduction potential (ORP) of reaction systems was

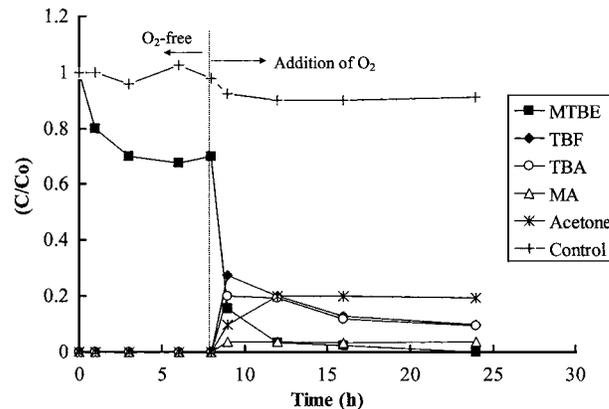


Fig. 4. Oxygen dependence of methyl *tert*-butyl ether transformation by bifunctional aluminum

measured when a multispike test of MTBE was conducted in a batch reactor during a period of 24 h. An Orion pH/mv meter equipped with a combination redox electrode was used for ORP measurement. The batch reactor containing 20 g/L of bifunctional aluminum was spiked with 0.4 mM of MTBE three times. As shown in Fig. 5, fast MTBE degradation occurred initially but reactions slowed down at the second time of MTBE spiking and eventually stopped at the third time. On the other hand, ORP measurement indicated that the system quickly reached reducing conditions (~-300 mV) within 6 h and then ORP increased slowly to about +360 mV at the end of the experiments. The changes of redox potential from reducing to oxidizing conditions indicated that aluminum is no longer serving as the effective electron donor. This suggests that no reaction of MTBE with bifunctional aluminum at the third spiking time is caused by lack of an effective reductant in the system. The failure of aluminum for serving as a reductant may be attributed to the consequence of inhibition of aluminum corrosion at higher pH because it was found that the pH solution increased to about 5.6 at the end of the experiment. Aluminum is resistant to corrosion in aqueous solutions with a pH in the neutral range from 4.5 to 8.5 (Davis 1999). The oxidative degradation of MTBE by bifunctional aluminum proceeded via the reductive activation of dioxygen that occurred only under reducing conditions.

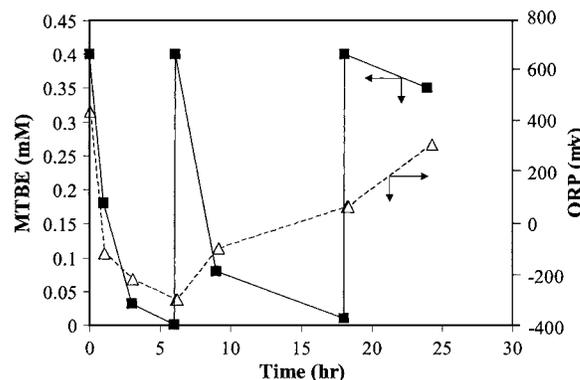


Fig. 5. Effect of oxidation reduction potential on methyl *tert*-butyl ether transformation by bifunctional aluminum

Conclusions

Technologies for the treatment of specific organic contaminants are being developed and proven; however, there are few technologies capable of treating both reductively degradable and oxidatively degradable contaminants together. In this work, oxidative and reductive degradation of contaminants with bifunctional aluminum in the presence of oxygen was found. Zero-valent aluminum served as a reductant while oxygen acted as an oxidant. This study demonstrates that bifunctional aluminum could be a promising reactive reagent for simultaneous treatments of a wide array of mixed contaminants. It could be used for both in situ and ex situ remediation of water contaminated with gasoline oxygenates and chlorinated solvents. Based on the dual functionality, a custom-designed bifunctional aluminum might become a potential strategy for the development of a contaminant-specific remedial system. For example, bifunctional aluminum can be modified by adding hydrogenation catalysts (e.g., Ni, Co, or Cu) onto the aluminum surface to promote its catalytic capability of the reduction. The aluminum-based bimetallics have been found for a better treatment of chlorinated solvents (Lien and Zhang 2002a). On the other hand, to better treat the contamination of gasoline oxygenates, bifunctional aluminum may be optimized toward the enhancement of the oxidizing capability. By combining the advantages of zero-valent metal technology with the reductive activation of dioxygen process, bifunctional aluminum opens a new avenue for environmental remediation where chemical treatments of oxidatively and reductively degradable contaminants together in the same system are possible.

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