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Technical Note

In Situ Colloidal MnO₂ Deposition and Ozonation of 2,4-Dinitrotoluene

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ABSTRACT

Laboratory experiments are presented that demonstrate a novel *in situ* semipassive reactive barrier for the degradation of 2,4 dinitrotoluene created by coating aquifer surfaces by deposition of colloidal MnO₂, which catalyzes ozone degradation and enhances contaminant oxidation. Ozone is added to the reactive barrier and is transported through the zone with the contaminants by existing hydraulic gradients. The communication presents the preliminary laboratory investigation demonstrating the viability of this method. Studies were conducted by coating Ottawa sand with colloidal MnO₂. Results show that concentrations of MnO₂ in the range of 0.2 mg/g can be deposited with no measurable change in hydraulic conductivity, that there is significant coverage of the sand material by MnO₂, and the deposition was not reversible under a wide range of chemical conditions. Ozonation of 2,4-dinitrotoluene in the presence of MnO₂-coated sand was demonstrated to result in pseudo-first-order degradation kinetics with respect to DNT with half-lives ranging from 28 to 22 min (at pH 6 and 7, respectively), approximately 25% faster than experiments performed in the absence of MnO₂.

Key words: colloid; manganese dioxide; deposition; ozone; dinitrotoluene; remediation; oxidation

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INTRODUCTION

CONTAMINATION OF SOILS AND GROUNDWATER remains a significant problem in the United States, in many cases because of the technical or economic infeasibility of remedial options. Development of remediation technologies that are robust and economically feasible are still needed to address numerous contaminated sites. This manuscript details the laboratory investigation of a novel technique to degrade recalcitrant organic compounds *in situ*. The technique is comprised of the engineered deposition of specific colloidal minerals *in situ* and subsequent oxidation of the organic compounds by ozone addition. The technology incorporates two aspects of current remediation systems: first, the concept of a reactive zone is used that permits the maintenance of water and contaminant flux passively, and second, an oxidation process is used, which in this case employs ozone. Ozone was selected because its aqueous decomposition as described by both Staehelin and Hoigné (1982) and Tomiyasu *et al.* (1985) results in the generation of hydroxyl radicals. Mineral deposition can be accomplished *in situ* using injection wells, which eliminate some of the difficulties associated with traditional reactive wall placement (difficult access to subsurface, deep contamination), and it offers the ability to be easily regenerated over time.

The concept for this remediation technique evolved from the general understanding that metal oxides play a central role in catalyzing hydrogen peroxide decomposition and contaminant oxidation (Pardieck *et al.* 1992; Miller and Valentine, 1999). Similarities likely exist to several aqueous treatment systems such as Fenton's reagent (Venkatadri and Peters, 1993), which exploit reactions involving other constituents to produce hydroxyl radical. Heterogeneous systems for organic contaminant degradation have focused primarily on the catalysis of hydrogen peroxide and ozone decomposition in the presence of prepared metal oxides and supported metal oxides (Gurol *et al.*, 1997; Valentine and Wang, 1998). For example, Al-Hayek *et al.* (1989) and Al-Hayek and Dore (1990) studied the oxidation of phenols by ozone and hydrogen peroxide in the presence of alumina-supported iron oxides and observed significant organic degradation. In another study, hydrogen peroxide addition to coarse sand effectively removed trichloroethylene and pentachlorophenol in a column reactor (Ravikumar and Gurol, 1994). Tyre *et al.* (1991) examined pentachlorophenol degradation in the presence of iron-silica sand-hydrogen peroxide mixtures and detected material specific decomposition and contaminant behavior. Manganese has also been shown to be an effective catalyst of ozone decomposition and organic compound removal (Andreozzi *et al.*, 1996; Gracia *et al.*, 1998). Andreozzi *et al.* (1997,

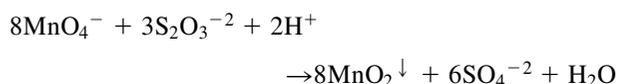
1998) suggested that both homogeneous and heterogeneous manganese-catalyzed reactions contribute to chemical oxidation of organics. Ma and Graham (1999) propose a mechanism involving enhanced contaminant removal based on catalysis by hydroxyl groups of the surface of the MnO₂. This body of work indicated the potential for success of an *in situ* remediation technique based on alteration of the mineralogy on aquifer media phases that are in contact with the contaminant/oxidant aqueous solution.

The major hypothesis of this work was that colloidal materials of specified mineralogy, deposited *in situ*, will act as a catalyst for chemical oxidant (e.g., ozone) decomposition resulting in formation of key oxygen radical intermediates capable of degrading specific contaminants (in this study 2,4-dinitrotoluene). There were three preliminary objectives that needed to be satisfied to confirm whether this hypothesis was viable. The first objective was to demonstrate that colloidal deposition could be performed without affecting the hydraulic conductivity of the existing aquifer. The second objective was to confirm that the added colloids will attach to the existing aquifer material, and will remain stable and attached (under expected conditions), and the third was to demonstrate that the deposited colloidal material would enhance organic degradation rates when exposed to ozone.

EXPERIMENTAL PROTOCOLS

Colloidal MnO₂ preparation

Colloidal MnO₂ was prepared according to the method of Tuncay *et al.* (1999). Briefly, a potassium permanganate solution is reduced using sodium thiosulfate according to the following stoichiometry:



The concentrations of KMnO₄, Na₂S₂O₃, and H₂SO₄ were 1.6 × 10⁻⁴ M, 2.24 × 10⁻⁵ M, and 1 × 10⁻⁵ M, respectively. This precipitation occurs at room temperature and pressure and a solution pH of 4.7. The precipitate was concentrated by centrifugation and the dispersion purified by successive dilutions. The median diameter of the prepared particles was 50 nm, as measured using light-scattering techniques (Coulter LS-230; Fullerton, CA), and the surface area was determined to be 270 m²/g by BET N₂ adsorption (Coulter SA-3100⁺).

MnO₂ deposition

The deposition of colloidal MnO₂ on a uniform size Ottawa sand (median size of 130 μm) was studied using

a column apparatus (diameter = 15.4 mm, length = 25.1 mm). The colloidal dispersion (concentration of 80 mg/L) was mixed just prior to the column entrance with a solution for electrolyte and pH adjustment (containing NaCl and either HNO₃ or NaOH). Effluent from the column was collected in a fraction collector and analyzed for colloidal MnO₂ concentration using a spectrophotometer at a wavelength of 500 nm. The mass of MnO₂ deposited was calculated from the breakthrough curves obtained. The production of coated sand for further experimentation with ozone and DNT was accomplished in a larger size column, with a diameter of 3.7 cm and length of 4 cm.

The characteristics of the MnO₂ deposition were studied using scanning electron microscopy (SEM). Data was obtained using a backscatter collector (a four-quadrant annular Si wafer detector, type 113A, made by GW Electronics Inc., with an Hitachi field emission SEM) to differentiate the deposited MnO₂ from the less dense sand support material.

DNT ozonation

Ozonation experiments were performed in a semibatch reactor system. The reaction vessel is a 500-mL graduated cylinder, which is placed on a stir plate set at a constant stirring level. Reactor system pH was maintained by using a single initial dose of hydrogen phosphate ($[\text{PO}_4^{-3}]_T \approx 13 \text{ mM}$) in contaminant degradation stud-

ies, and by NaOH addition in the ozone decomposition rate experiments. Ozone gas was diffused into the main reactor vessel at a rate of $Q_{\text{gas}} = 4 \text{ L/h}$ using a Pyrex Brand[®] gas dispersion tube with a fritted concentric disc and stem. The ozone molar feed rate ($m_{e(\text{ozone})}$) was consistent for all experiments at $6.35 \times 10^{-3} \text{ mol/min}$. Ozone gas phase was measured photometrically at $\lambda = 294 \text{ nm}$ using an extinction coefficient for gaseous ozone at 294 nm of $\epsilon = 225 \text{ M}^{-1} \text{ cm}^{-1}$ (Langlais *et al.*, 1991). Aqueous ozone residual concentration was determined using Standard Method 4500-O₃ B. Indigo Colorimetric Method (Eaton *et al.*, 1995).

2,4-Dinitrotoluene was monitored using a Shimadzu high-performance liquid chromatograph (HPLC) equipped with a photo diode array detector and a Discovery[™] C8 (15 cm × 4.6 mm i.d., 5 μm) HPLC column. The mobile phase consisted of HPLC grade water with 1% acetic acid and acetonitrile with 1% acetic acid operating in a low-pressure mix configuration and mobile phase gradient system of 5:95 (v:v) at the time of the injection and 100:0 after 15 min of operation.

RESULTS AND DISCUSSION

A number of column experiments were conducted to investigate the characteristics of deposition by observation of breakthrough curves as a function of pH and fluid

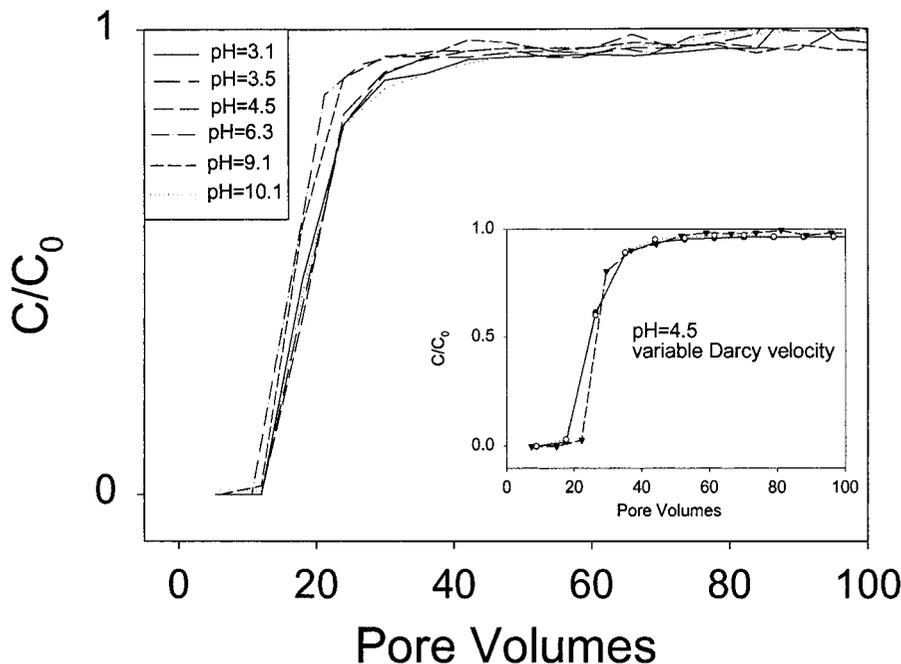


Figure 1. Breakthrough curves for MnO₂ introduced to a column containing Ottawa sand under variable pH and velocity. MnO₂ (80 mg/L) 10^{-3} M NaCl , Darcy velocity of 2.98 m/day. Inset: Darcy velocity of 0.25, 2.98, and 5.96 m/day.

velocity. All of the experiments were conducted in the presence of 10^{-3} M NaCl background electrolyte. Interestingly, as shown in Fig. 1, there was little dependence of deposited mass with pH, indicating favorable deposition for the range of conditions shown. Similar results were obtained for the variation of Darcy velocity at constant pH: no significant changes in breakthrough time were noted for Darcy velocities ranging from 6.9×10^{-3} to 2.9×10^{-4} cm/s (5.96 to 0.25 m/day), although a small delay in breakthrough is noted for the lowest velocity, as would be expected. The average mass of MnO_2 deposited was approximately 0.2 mg/g, as determined by integration of the breakthrough curves. These results suggest that MnO_2 may be a robust phase in terms of its ability to be deposited in formations, to the extent that the Ottawa sand used in these experiments is representative of aquifer media.

Deposition experiments were also conducted using constant head reservoirs to permit periodic measurement of the hydraulic conductivity of the media. Hydraulic gradients of 1.25 and 2.4 were used in deposition and measurement of hydraulic conductivity. In all experiments there was no measurable change in the hydraulic conductivity of the medium. A typical hydraulic conductivity for the media packed in the column in these experiments was 0.005 cm/s (which varied slightly between experiments). Changes in hydraulic conductivity is an important consideration, as any significant increase in hydraulic conductivity would likely preclude the use of this technology for placement of a reactive barrier.

The coverage obtained by depositing the MnO_2 onto Ottawa sand was assessed by scanning electron microscope (SEM) imaging. Figure 2 shows a typical sand grain coated with colloids. Collecting backscatter data allowed the discrimination of the heavier metal oxide particles, which show up as bright spots on the image in Figure 2, from the less dense SiO_2 . Figure 2 demonstrates that there is fairly consistent coverage of the sand particles, although the sand surface clearly is still available and in contact with the solution phase. Image analysis was conducted on the sand grain in Fig. 2, and indicated that 19.4% of the sand surface was covered by colloidal metal oxide particles.

The reversibility of the deposition was studied by first depositing MnO_2 until breakthrough was achieved, then stopping the flux of colloidal particles into the column while maintaining flow, ionic strength, and pH conditions. Subsequent to the observation that no colloids were exiting the column reactor, the pH and ionic strength of the influent were independently varied (pH from 2.5 to 10 with background electrolyte followed by introduction of distilled, deionized water). No release of colloidal material was measured, indicating a stable coating was achieved under the conditions investigated. Stability was also observed qualitatively during ozonation experiments, which was in direct contrast to experiments in which the authors precipitated MnO_2 directly on the sand surface. In the direct precipitation experiments, ozonation resulted in what appeared to be almost complete release of manganese from the porous medium. Con-

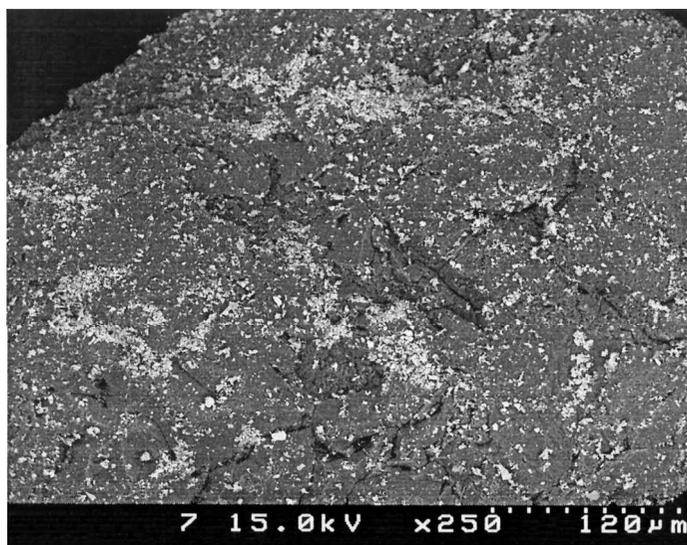


Figure 2. SEM backscatter image showing metal oxide colloids (bright areas) deposited on Ottawa sand grain (darker background material).

Table 1. Pseudo-first-order rate constants (k_{obs}) with 95% confidence interval

Description	k_{obs} (min^{-1})
DNT degradation in the presence of MnO ₂ at pH 6.0	$2.5 \pm 0.1 \times 10^{-2}$
DNT degradation in the presence of MnO ₂ at pH 7.0	$3.1 \pm 0.6 \times 10^{-2}$
Ozone decomposition in the presence of MnO ₂	$16.8 \pm 3.7 \times 10^{-2}$
Ozone decomposition in the absence of MnO ₂	$6.2 \pm 1.1 \times 10^{-2}$
DNT degradation in the absence of MnO ₂	$1.9 \pm 0.3 \times 10^{-2}$

versely, no release was visually observed from the deposited colloidal coating method.

DNT ozonation

The final objective of this study was to assess whether the manganese dioxide coating procedure would result in a material capable of catalyzing DNT degradation in the presence of ozone. The general hypothesis provided in the introduction of this paper relies on the assumption that enhanced DNT degradation will occur based on enhanced radical generation. DNT was selected as the model contaminant because it has a slow reaction rate with ozone directly, but should react well with hydroxyl radical (Buxton *et al.*, 1988), a reaction intermediate of aqueous ozone decomposition. The first experiment was designed to compare manganese dioxide-coated sand (MnO₂-sand) catalyzed ozone DNT degradation to direct ozonation at pH 6.0. MnO₂-sand resulted in an observed

first-order DNT degradation rate (k_{DNT}) that was approximately 25% faster, based on the regression value, than ozone in the absence of MnO₂-sand (Table 1). Andrezzi *et al.* (2000) also observed enhanced organic degradation rates by ozone in the presence of manganese dioxide at near neutral pH; however, the manganese was colloidal in nature, and was not supported. A total of seven DNT degradation by-products were monitored; however, dinitrobenzoic acid was the only by-product observed above detection limits through the course of the experiment, which is consistent with findings in other hydroxyl radical generating systems (Ho, 1986).

In an effort to confirm the surface was catalyzing ozone decomposition and ultimately radical generation, experiments were performed where ozone decomposition was measured both in the presence and absence of MnO₂. The pseudo-first-order rate constant for ozone alone was 37% slower than ozone decomposition in the presence of MnO₂. Actual values with 95% confidence intervals ap-

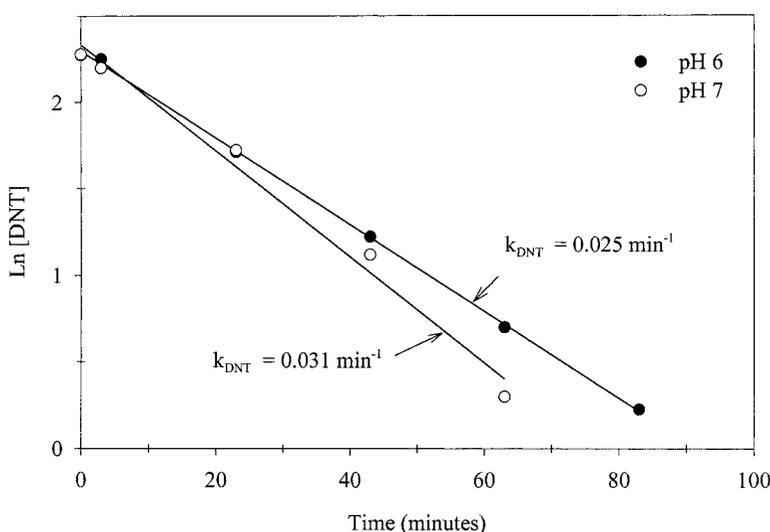


Figure 3. Observed first-order DNT degradation at pH 6.0 ± 0.2 and pH 7.0 ± 0.2 . Semibatch reactor apparatus, $[\text{DNT}]_0 = 2.65 \times 10^{-5}$ M, $[\text{MnO}_2\text{-Sand}] = 10$ g/L, $Q_{\text{gas}} = 4$ L/h, $m_{e(\text{ozone})} = 1.47 \times 10^{-5}$ mol/min, and $[\text{PO}_4^{-3}]_{\text{Total}} = 13$ mM.

pear in Table 1. It is important to point out the pHs of these experiments were controlled by NaOH addition and not by phosphate buffer. Studies have been conducted indicating phosphate may play a role in advanced oxidation processes, although specific mechanisms for the role of phosphate in ozone/metal oxide systems have not been elucidated (Miller and Valentine, 1999; Valentine and Wang 1998; Andreozzi *et al.*, 2000).

A third experiment was run to evaluate the influence of pH. Figure 3 illustrates the observed first-order DNT degradation rate at pH 6.0 and 7.0 in the presence of MnO₂-sand (10 g/L). The degradation rate constant was 24% faster at pH 7.0, consistent with known aqueous ozone decomposition mechanisms, which show ozone decomposition to be initiated via OH⁻ (Chelkowska *et al.*, 1992). Actual values with 95% confidence intervals appear in Table 1. Whereas these results suggest that MnO₂ may act as a catalyst for both O₃ decomposition and DNT degradation, experiments are needed to elucidate the stability of the coating surface vs. solution reactions and DNT degradation due to MnO₂-sand catalyzed reactions from the direct catalyzed ozonation degradation pathway.

CONCLUSIONS

The experiments presented in this research indicate the potential feasibility of a novel *in situ* remediation technique: a semipassive reactive barrier wall that is put in place by the engineered deposition of colloidal catalyst particles. It was demonstrated that MnO₂ was effectively deposited at a concentration of approximately 0.2 mg/g, which resulted in coverage of approximately 19% of the sand surface. It was also shown that this deposition was not reversible under a range of chemical conditions, and that hydraulic conductivity was not measurably reduced.

Furthermore, manganese dioxide, in the concentrations deposited, was effective in enhancing DNT degradation kinetics compared with direct ozonation. Additional research is needed to examine coating procedures to achieve a greater surface coverage of manganese, which would likely have a direct bearing on degradation rates. This remediation technique is likely suitable for a range of recalcitrant organic compounds; however, additional research is needed to demonstrate its efficacy with other contaminants, in natural aquifer materials, and under *in situ* conditions.

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