

Characteristics of Potassium Permanganate Encapsulated in Polymer

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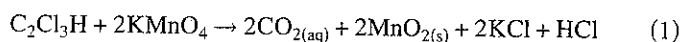
Abstract: Potassium permanganate was encapsulated in various polymers to create microcapsules with slow-release properties. Batch tests were conducted to evaluate the rates at which the microcapsules release permanganate. The release histories of 18 different polymer formulations varied strongly, but average initial release rate was 2.70 g KMnO₄ released g KMnO₄ initial⁻¹ d⁻¹, and the release rate typically decreased with time. The total duration of release ranged from 3 to 80 days, with an average of 27 days. In other batch tests trichloroethene (TCE) was degraded to below detectable amounts by the microcapsules. The degradation rate for TCE was three to four times faster during the initial reaction period than predicted based on permanganate release rates. There appear to be several promising environmental applications for this method of creating a slow-release oxidant.

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Introduction

Potassium permanganate (KMnO₄) is a versatile chemical oxidant that can degrade volatile and semivolatile organic compounds in soil and groundwater (e.g., Schnarr et al. 1998; Siegrist et al. 1999; Gates-Anderson et al. 2001; Siegrist et al. 2001), and it has gained particular attention for its ability to degrade chlorinated ethenes (Walton et al. 1991; Vella and Veronda 1992; Siegrist et al. 2001). The oxidation reaction between permanganate and trichloroethene (TCE) involves cleaving the double carbon bond in TCE to yield CO₂, manganese dioxide (MnO₂), potassium chloride (KCl), and hydrochloric acid (HCl) (Yan and Schwartz 1998), according to



The complete reaction involves intermediate steps and is described in more detail by Yan and Schwartz (2000) and Huang et al. (1999).

KMnO₄ is also commonly applied to the treatment of wastewater and drinking water. It has been used to oxidize trihalomethane precursors (Colthurst and Singer 1982) and manganese (Carlson and Knocke 1999) and to treat low concentrations of

phenols (Vella et al. 1990) in water. Other uses include removal of organics and color from a variety of industrial and domestic wastewaters (Walton et al. 1991), as well as improving taste and reducing odors in drinking water (Cherry 1962).

Field tests where KMnO₄ has been used for remediation have shown promise (Siegrist et al. 2001) but they also have brought to light several drawbacks. One problem encountered is difficulty controlling distribution of oxidant in the subsurface (ORNL 1997; Schnarr et al. 1998). This occurs because permanganate is typically injected as an aqueous solution and it can move along preferential pathways in the subsurface. Nonuniform distribution of oxidant may result in zones of incomplete contaminant degradation. Another factor is insufficient oxidant transport from the point of subsurface delivery that can result from high soil oxidant demand (Cline et al. 1997; McKay et al. 1998). Additionally, formation of MnO₂ (a product of the reaction between KMnO₄ and TCE) can cause further remediation difficulties by reducing the hydraulic conductivity of the soil in the treatment zone, thus limiting fluid movement through the area (Drescher et al. 1998; Schroth et al. 2001). Field tests have also shown that KMnO₄ oxidation can influence the mobility of certain metals (such as cadmium, chromium, copper, lead, manganese, mercury, nickel, and zinc) (Siegrist et al. 2001; Crimi and Siegrist 2003).

Reactive solids can be used to create reactive barriers that passively degrade contaminants in situ, but the properties of permanganate make it poorly suited to forming reactive barriers. Raw permanganate is highly soluble, so it readily dissolves and becomes mobile in ground water. One approach for creating a reactive barrier in a fixed location is to inject granules of permanganate suspended in a clay-rich slurry (Siegrist et al. 1999). That approach is best suited to low permeability media because the clay slurry may create low permeability conditions that divert groundwater where the barrier is created in a relatively permeable formation.

A standard method for placing solids in subsurface reactive barriers is to suspend them as granules in guar gum gel. This approach has been used to create horizontal reactive layers by filling hydraulic fractures with reactive media and for holding

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open vertical trenches while they are filled with reactive media (Murdoch et al 1997; Siegrist et al 1999). This cellulose-based material readily breaks down and can be removed from pores to leave the permeability of the solids unaffected. Unfortunately, raw permanganate destroys guar gel and renders it unable to suspend solids, so the methods for placing solids that make use of guar gel are ineffective when used with raw permanganate.

Permanganate also vigorously reacts with tissue. As a result, raw permanganate must be handled with care, and it presents particular safety concerns because fine-grained particles can become air-borne and inhaled (Carus Chemical Company 2000).

One approach to address some of these problems is encapsulating grains of potassium permanganate in an inert shell. When immersed in water, the shell isolates grains in the core and prevents immediate dissolution. The core material diffuses out through the shell and is released at the surface of the capsule. Water also diffuses into the capsule and can react with the core material to affect the release rate. The rate at which these processes occur depends on the diffusivity of the core compound in the shell material and the diffusivity of water in the shell material, as well as the thickness of the shell and the distribution of the core granules within the capsules (Pothakamury and Barbosa-Cánovas 1995).

Microencapsulated materials have already seen some applications in soil and groundwater remediation. Perhaps the first application of this technology to in situ remediation was described by Vesper et al. (1994), who encapsulated percarbonate in polyvinylidene chloride to create a slow-release oxygen source for bioremediation. A phosphate buffer was encapsulated in polymer for pH control during denitrification of contaminated groundwater and sediment (Rust et al. 2000, 2002). Iron was encapsulated in a cross-linked alginate gel as a component in Fenton photo-assisted degradation of aromatic compounds (Fernandez et al. 2000). Bacterial cells have been encapsulated in polymer to enhance bioremediation of gasoline hydrocarbons (Moslemy et al. 2002).

In this work, KMnO_4 was encapsulated in polymers to create microcapsules (diameters ranging from 60 to 2,000 μm) that slowly release permanganate to degrade organic compounds in water. One potential application for the microcapsules is to provide additional options for delivering permanganate in situ. Slow-release granules could be injected into hydraulic fractures (Murdoch et al. 1997) or used to fill trenches or boreholes to create in situ reactive barriers. Raw KMnO_4 is too soluble to form a reactive barrier that persists for any substantial duration, but microcapsules could possibly extend the life of an oxidative barrier enough to have practical applications. In addition to improving processes, the coated microcapsules may be safer to handle than raw KMnO_4 .

The purpose of this paper is to present the methods and results of laboratory research to examine the feasibility of creating permanganate microcapsules for treatment of TCE contaminated water. This was evaluated in two types of batch tests in which microcapsules were immersed in water. The first set determined the release rate of permanganate by measuring its concentration in the water as a function of time. The second set measured the degradation rate of TCE in water containing a suspension of microcapsules as a function of time.

Materials and Methods

Microcapsules consist of at least two materials, a core and a shell. The core material used for microcapsules in this work is granular,

technical-grade KMnO_4 (Carus Chemical Company, Peru, Ill.). The shell materials consist of various blends of waxy polymers. The shell compounds were selected because we anticipated they would be unaffected by permanganate and have relatively low diffusivities to water-soluble compounds. The most abundant polymers in the blends are Boler wax, Piccolyte resin S115, and Epolene C-16. Small batches of a variety of other waxes were also evaluated, including a chlorinated wax (Chlorez 700), which was used because it was expected that chlorinated solvents would readily partition into this material. A total of 19 samples were evaluated [details of the polymer blends are in Ross (2001)].

Microcapsules were fabricated using a spinning disk apparatus (Pothakamury and Barbosa-Cánovas 1995). A slurry of KMnO_4 and wax was created by heating the material above the melting point of the wax and dispersing the solid particles in the molten wax using a sonicator. The slurry was introduced along the axis of the spinning disk. It flowed along the surface of the disk and then formed droplets as the slurry left the edge of the disk. The droplets cooled, solidified, and were collected after they reached the ground. This technique can be readily scaled up to create large quantities of material for industrial applications.

The encapsulation process produced two types of microcapsules. One type had a core that consisted of a single grain of KMnO_4 enveloped in a polymer shell; it will be referred to as SGC (single grain core) material. The other type had multiple grains (5–10) of KMnO_4 in the core and it will be referred to as MGC (multiple grain core) material. SGC material was created by spinning the disk relatively rapidly, which created small droplets at the edge of the disk, whereas MGC material was created by slowing the rotation rate and increasing the droplet size. The grain size of the SGC material ranged from 60 to 1,000 μm , whereas the MGC material was coarser but more uniform, ranging from 600 to 2,000 μm . The mass ratio of KMnO_4 to shell material in the microcapsules ranged from 0.25 to 0.50.

Permanganate Release Tests

Batch release tests were conducted on all samples by placing 0.2 g of microcapsules in 250 mL amber glass bottles containing 150 mL of distilled deionized (DDI) water. The bottles were agitated on an orbital shaker at room temperature (22–24°C) and the concentration of KMnO_4 in the water was determined as a function of time. The bottles were sampled once per hour for the first 3 h and at least once every 2 days thereafter. Measurements continued until the KMnO_4 concentration changed by less than 5.0 mg L^{-1} over 10 days. Samples were obtained by pipetting 0.1–1.0 mL from each bottle and diluting with DDI water. KMnO_4 was measured with a Hach DR/2010 spectrophotometer, which was calibrated using the same technical grade KMnO_4 present in the microcapsules.

The release of permanganate was quantified based on time plots of the concentration ratio C_r , defined as $C_r = CV/M$, where C = concentration of permanganate in the water, M = mass of permanganate added to the serum bottles, and V = volume of water in the serum bottles. The release for most of the tests began with C_r increasing roughly as a linear function of time, followed by a decreased rate of release as C_r approached a maximum at the end of the test.

The release rate was characterized by four parameters (Fig. 1). The slope of C_r as a function of time represents the release rate, so the initial rate of release k_0 was calculated by performing a linear regression on the first three data points of the release data. C_r reached steady values of slightly less than 1.0 at the end of

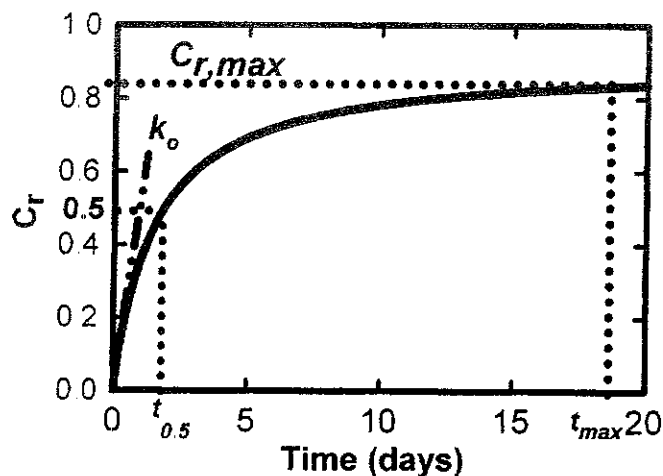


Fig. 1. Concentration ratio as a function of time in an idealized release test, showing $C_{r,max}$, k_0 , $t_{0.5}$, and t_{max}

most tests. As a result, C_r at the end of each test was assumed to be the maximum concentration ratio ($C_{r,max}$) that can be achieved by that material during batch tests. A $C_{r,max}$ value significantly less than 1.0 indicates a sink for the permanganate. The duration of permanganate release was also of interest, so the tests were further characterized by $t_{0.5}$, the time required to release half of $C_{r,max}$, and t_{max} , the time required to reach $C_{r,max}$ (Fig. 1)

Permanganate Release Models

Three functions were used to approximate the release rate behaviors from the batch tests (Ross 2001). One function was based on an analysis of diffusion from spheres of solute dispersed in a matrix, as described by Desai et al. (1965) and Kydonieus (1980). They assume that (1) a pseudo-steady state exists; (2) the $KMnO_4$ particles are small compared to the average distance of diffusion; (3) the diffusion coefficient of the matrix is constant; and (4) a perfect sink condition exists in the external media (i.e., concentration equals zero). The final concentration was slightly less than expected, so the results of Kydonieus (1980) were modified to give

$$t = \frac{Ar^2}{2SD} \left[1 - (C_r/C_{r,max})^{2/3} - \frac{2}{3}(C_r/C_{r,max}) \right] \quad (2)$$

where S =solubility of the solute in the matrix, D =diffusivity of the solute through the matrix, A =initial concentration of the solute in the matrix, and r =radius of the microcapsules

Another function to predict the release of permanganate was developed by assuming one-dimensional (1D) diffusion occurred from a core containing a saturated solution of $KMnO_4$ through a shell with diffusivity, D , and into water with concentration, C_w . Based on these assumptions it follows (Ross 2001) that

$$C_w = C_{sat} (1 - e^{-(3DHw/Tr\gamma V_w)t}) \quad (3)$$

where H =partitioning coefficient for $KMnO_4$ between the shell and the water (dimensionless), w =initial mass of $KMnO_4$ in the solid phase, t =time, T =thickness of the shell, r =radius of the core, γ =unit weight of the particles ($g\ cm^{-3}$), and V_w =volume of water in the bottle. C_{sat} =63.8 $g\ L^{-1}$ at 20°C for $KMnO_4$ (Weast 1987)

The functions described above are relevant to processes that were expected to control release from the microcapsules, and in-

deed, all of the constants are related to physically relevant quantities. An empirical function was also used to characterize release of permanganate from the microcapsules

$$C_r = \frac{C_{r,max}t}{t_{0.5} + t} \quad (4)$$

Trichloroethene Degradation and Adsorption Tests

TCE degradation tests were conducted by combining 0.03–0.2 g of microcapsules and 1.0–7.0 μL of reagent grade TCE (Fisher Scientific, Fairlawn, N.J.) with 20–100 mL of DDI water in a 160 mL serum bottle, and then agitating the bottle and measuring the concentration of TCE as a function of time. Initial TCE concentrations ranged from 290 to 700 μM (38–92 $mg\ L^{-1}$), which is in the higher range of TCE concentrations typically found in contaminated groundwater. The concentration of TCE chosen for the degradation tests was a function of the mass of microcapsules required to get a representative sample and the detection limit for TCE. The mass of microcapsules was selected to ensure that enough permanganate was available to completely degrade the TCE in the vial, based on the reaction stoichiometry and the results of the release tests, but excessive permanganate loading was avoided. The molar ratio of permanganate to TCE ranged from 3.3 to 6.8 in the experiments, compared to the stoichiometric ratio of 2.0 that was required for complete oxidation [Eq. (1)].

After adding the microcapsules, the serum bottles were capped with Teflon-faced red rubber septa and 1.0–7.0 μL of neat TCE was added. The first headspace measurement for TCE was made 20–30 min later; subsequent measurements were made at least once every 2 days until the TCE was below detection. Controls consisted of serum bottles with water and TCE present, but no microcapsules. All treatments were run in triplicate.

The extent of TCE adsorption to representative shell materials (without $KMnO_4$ present) was determined by placing samples in vials with four different concentrations of TCE in DDI water. TCE concentrations were monitored for 30 days to ensure that equilibrium was reached. Controls consisted of vials with TCE and water but no sorbent. The extent of adsorption was evaluated based on the Freundlich isotherm for a single solute (LaGrega et al. 1994), which includes coefficients reflecting the magnitude of sorption (K_f) and the degree of nonlinearity for the isotherm ($1/n$).

Analytical

The total mass of TCE present in serum bottles was determined using a headspace analysis procedure developed by Gossett (1987). The aqueous phase concentration of TCE was calculated from the total mass present assuming equilibrium partitioning between the headspace and liquid (Vercé et al. 2000). The method detection limit was 35 $\mu g\ L^{-1}$. Permanganate was measured by diluting 0.1-mL samples with up to 3.0 mL of DDI water, homogenizing with a vortex mixer, and filtering through 0.1 μm nylon syringe filters to remove MnO_2 solids. Absorbance was measured at 528 nm with a Beckman DU-640 spectrophotometer in a 100 μL cuvette. The detection limit was 0.5 $mg\ KMnO_4\ L^{-1}$. Chloride was measured with a combination electrode (Orion, model 9617BN). An ionic strength adjustor (0.2 mL of 5 M $NaNO_3$) was added to samples. The detection limit was 0.2 mM Cl^- . Potassium was measured using a Waters 717 Ion Chromatograph plus autosampler with an HPLC pump and conductivity detector. A Waters IC-Pak Cation M/D column was used with a

Table 1. Parameters Describing Release from Microcapsules

Sample	Type	$t_{0.5}$ (d)	t_{max} (d)	$C_{r,max}$	k_0 (g g ⁻¹ d ⁻¹)	SD [Eq. (2)] (g cm ⁻¹ s ⁻¹)	$\frac{3DH_w}{Tr\gamma V_n}$ [Eq. (3)] (d ⁻¹)	DH [Eq. (3)] (cm ² s ⁻¹)
19-230	SGC	0.020	6.3	0.80	9.41			
19-231	SGC	0.055	6.3	0.60	7.63			
19-232	SGC	0.060	6.3	1.0	7.61			
19-233	SGC	0.042	5.4	1.0	8.81			
19-234	SGC	0.044	6.3	0.81	7.68			
19-235	SGC	0.178	3.0	0.83	3.07			
19-236	SGC	0.339	12	0.86	2.19			
19-306	MGC	1.69	6.8	0.88	0.15	5.0×10^{-9}	1.5×10^{-3}	7.7×10^{-9}
19-307	MGC	7.93	26	0.86	0.03	1.3×10^{-9}	0.4×10^{-3}	1.7×10^{-9}
19-308	MGC	12.7	36	0.95	0.10	1.3×10^{-9}	1.0×10^{-3}	5.4×10^{-9}
19-546	MGC	5.26	36	0.95	0.19	1.2×10^{-9}	1.9×10^{-3}	1.0×10^{-9}
19-547	MGC	3.29	42	0.80	0.20	2.2×10^{-9}	2.0×10^{-3}	1.0×10^{-9}
19-548	MGC	2.40	36	0.94	0.29	3.0×10^{-9}	2.9×10^{-3}	1.5×10^{-9}
19-549	MGC	6.73	80	0.88	0.21	1.3×10^{-9}	2.1×10^{-3}	1.1×10^{-9}
19-550	MGC	4.38	46	0.93	0.22	1.6×10^{-9}	2.2×10^{-3}	1.1×10^{-9}
19-551	MGC	1.84	42	0.92	0.38	3.0×10^{-9}	4.1×10^{-3}	2.1×10^{-9}
19-552	MGC	3.01	18	0.94	0.21	2.0×10^{-9}	2.1×10^{-3}	1.1×10^{-9}
19-553	MGC	6.36	66	0.94	0.22	1.2×10^{-9}	2.2×10^{-3}	1.1×10^{-9}
Average		3.13	26.7	0.88	2.70	2.1×10^{-9}	2.0×10^{-3}	1.0×10^{-9}
Standard deviation		3.54	22.8	0.09	3.64	1.2×10^{-9}	9.1×10^{-3}	4.7×10^{-9}

Note: SGC=single grain core; and MGC=multiple grain core

3 mM HNO₃ and 0.1 mM [ethylenedinitrilo]-tetraacetic acid (EDTA) eluent. The detection limit was 0.2 mg K⁺L⁻¹.

Results

The SGC samples released permanganate more rapidly and over a shorter duration than the MGC samples. The average k_0 for SGC material was 6.2 (± one standard deviation of 2.8) grams of KMnO₄ released per g KMnO₄ initial per day, ranging from 2.2 to 8.8 g KMnO₄ released g KMnO₄ initial⁻¹ d⁻¹ (Table 1). The average $t_{0.5}$ value was 0.11 (±0.11) d, ranging from 0.020 to 0.339 d. The average total time of release as characterized by t_{max} was 6.6 (±2.8) days, ranging from 3.0 to 12 days. The average $C_{r,max}$ value was 0.84 (±0.14) d, ranging from 0.60 to 1.0.

The average k_0 for the MGC batch tests was 0.2 (±0.09) g KMnO₄ released g KMnO₄ initial⁻¹ d⁻¹, more than 30 times slower than for SGC samples (Table 1). The average $t_{0.5}$ value was 5.1 (±3.3) d, more than 45 times longer than the SGC samples, and the average value of t_{max} was 39 days, which was considerably longer than for the SGC samples (Fig. 2). The average $C_{r,max}$ value was 0.91 (±0.05), ranging from 0.80 to 0.95.

There was substantial variability in permanganate release behaviors among the MGC material (Fig. 2). For example, k_0 varied by a factor of 12, ranging from 0.3 to 3.8 g KMnO₄ released⁻¹ g KMnO₄ initial⁻¹ d⁻¹, and $t_{0.5}$ ranged from 1.7 to 12.7 days. There was even more variability in t_{max} values, which ranged from 6.8 to 80 days.

Batch release results were simulated using the two models defined by Eqs. (2) and (3) and the empirical model in Eq. (4) (Ross 2001). This was accomplished by adjusting values of parameters to minimize the sum of squared residuals between the

predicted and observed concentrations (Fig. 3). The best fit was obtained with the empirical model, based on an average R^2 of 0.957 for the release rates of MGC material, and 0.885 for the SGC material (Table 1).

The other two models [Eqs. (2) and (3)] were able to represent the release rate behaviors over a limited range of C_r . The form of Eq. (2) was valid in the range of $0 < C_r < 0.8 C_{r,max}$, but errors were significant when C_r approached $C_{r,max}$. Eq. (3) was valid over $0 < C_r < 0.5 C_{r,max}$, but errors also occurred as C_r approached $C_{r,max}$. These errors decreased the R^2 values to less than

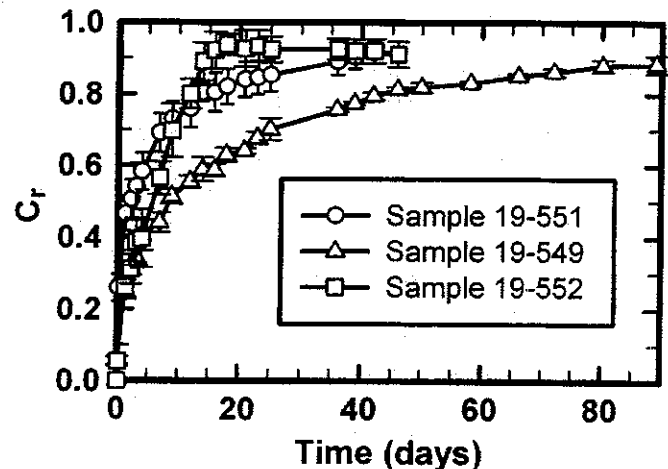


Fig. 2. Concentration ratio as a function of time for three encapsulated samples. Symbols are the average, and error bars are the standard deviation of triplicate measurements

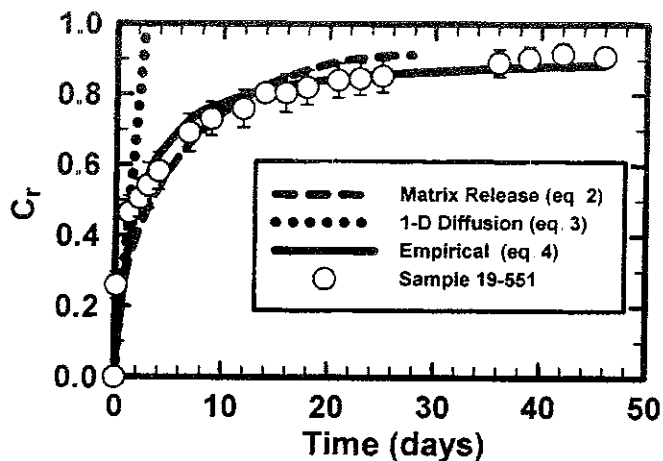


Fig. 3. Models fitted to data from a batch release test using sample 19-551. Symbols are the average, and error bars are the standard deviation of triplicate measurements.

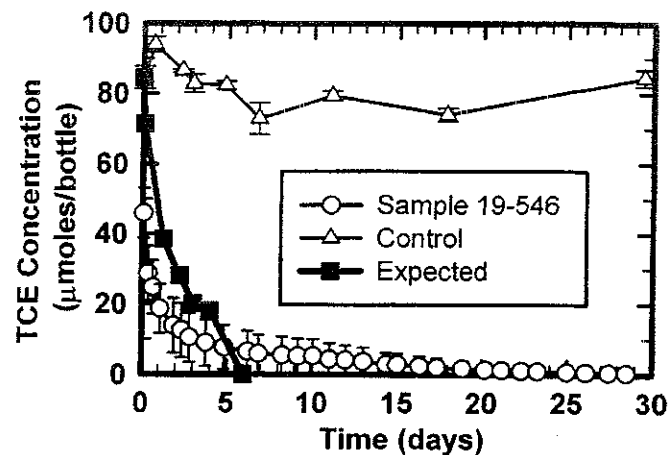


Fig. 4. Observed trichloroethene (TCE) concentrations during batch degradation tests with microcapsules 19-546, and during a control test with no microcapsules. Expected TCE concentrations are based on results from release tests. Symbols are the average, and error bars are the standard deviation of triplicate measurements.

those obtained using Eq. (4) (Ross 2001). Parameter estimates were obtained by fitting the early portions of the data set (Table 1). The curve-fitting procedure, combined with independent measurements or estimates of A and r , was used to solve for SD in Eq. (2). A similar procedure was used to estimate DH by fitting Eq. (3). Independent measurements of the diffusivity were unavailable, however, a range of values for D of 2×10^{-9} to $9 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ was used as an estimate. This gave a range for the solubility (S) between 2.3×10^{-3} and $10 \times 10^{-3} \text{ g cm}^{-3}$ (Table 1). The partitioning between shell material and water, H , ranged from 5.2×10^{-3} to 23×10^{-3} (Table 1). The H values were consistent with data reported by Cussler (1997).

Trichloroethene Degradation Tests

Batch tests were conducted to evaluate the degradation of relatively high concentrations of TCE over several days to weeks. The SGC microcapsules were not used in this set of tests because they released permanganate too quickly, whereas the MGC material was effective for as long as 38 days. It is likely that degradation was effective for an even longer period, but TCE could not be detected after 38 days so the degradation capacity was not evaluated after this time.

TCE degradation tests were designed using results from the batch release tests. It was assumed that permanganate would be released during the degradation tests at the same rate as during the batch release tests. It was also assumed that TCE would degrade stoichiometrically and therefore the permanganate release rate behavior could be used to predict the TCE degradation rate behavior. The mass of microcapsules added to each sample bottle was selected to exceed, by several times, the mass required to degrade the TCE based on reaction stoichiometry. Typically, the release data indicated that TCE should be completely degraded within approximately 1 week based on the masses of microcapsules that were added.

The predicted degradation rate behaviors were reasonably accurate in some cases, but not for others (Figs. 4 and 5). This is significant because it suggests that the mechanism by which the TCE is being degraded differs from a simple diffusive release from the microcapsules. TCE degradation always occurred at a relatively high rate upon exposure to microcapsules, followed by a period of slower degradation. This was an expected result be-

cause the rate of release of permanganate slowed with time. The length of time for TCE to degrade below the detection limit varied considerably.

MnO_4^- and MnO_2 were both identified visually in solution (MnO_4^- as a translucent purple solution, MnO_2 as fine-grained brown solids) during the degradation of TCE. MnO_4^- was seen early in the tests (1–3 d), indicating that some permanganate was reaching the water where it could react with TCE in solution, and MnO_2 was present in increasing amounts throughout the reaction period.

The rate of TCE degradation during the first few days was predicted fairly well using the batch release data for samples 19-307 and 19-308 and initial TCE concentrations of 38 mg L^{-1} . However, the release data lead to predictions that TCE should be completely degraded in approximately 1 week, but it took more than 3 weeks to completely degrade TCE. In another suite of tests in which TCE concentrations were 92 mg L^{-1} (for samples 19-

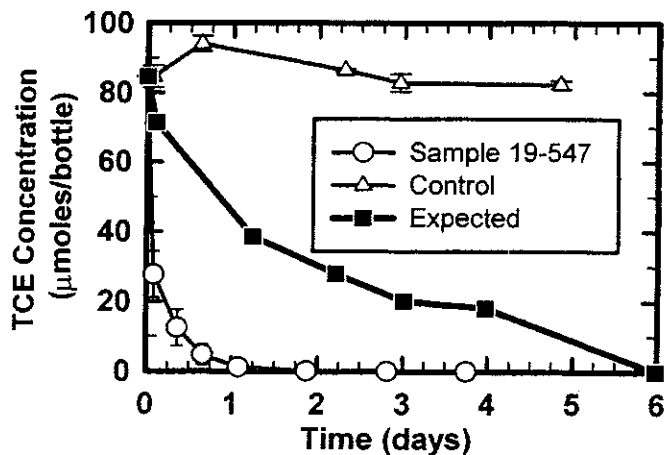


Fig. 5. Observed trichloroethene (TCE) concentrations during batch degradation tests with microcapsules 19-547, and during a control test with no microcapsules. Expected TCE concentrations are based on results from release tests. Symbols are the average, and error bars are the standard deviation of triplicate measurements.

Table 2. Observed and Predicted Trichloroethene Degradation Parameters

Sample	$t_{0.99}$ observed	$t_{0.99}$ predicted	IDR observed	IDR predicted	IDR observed/ IDR predicted
19-307	30.9±4.44	7.57±0.34	0.07±0.037	0.12±0.011	0.55
19-308	23.0±3.88	5.48±1.89	0.19±0.047	0.28±0.044	0.66
19-546	18.5±13.1	2.74±0.25	2.12±0.272	0.66±0.15	3.2
19-547	1.29±0.35	2.28±0.30	1.97±0.119	0.53±0.058	3.7
19-548	24.2±9.10	4.87±1.34	2.77±0.111	0.82±0.00	3.4
19-549	5.96±3.34	2.57±0.33	1.67±0.310	0.44±0.019	3.8
19-550	20.3±3.58	5.85±0.65	1.78±0.158	0.49±0.061	3.6
19-551	6.05±4.99	5.69±1.35	3.78±0.237	0.92±0.083	4.1
19-552	5.51±1.90	3.41±1.35	1.71±0.050	0.44±0.054	3.9
19-553	19.3±7.15	8.34±1.07	2.00±0.193	0.49±0.11	4.1

Note: $t_{0.99}$ = average time (\pm standard deviation) to remove 99% (d); and IDR = initial degradation rate [average (\pm standard deviation)]

546, 19-547, 19-548, 19-549, 19-550, 19-551, 19-552, and 19-553), the degradation rate was much faster than expected during the first 3–6 d, but it diminished after that. In two of those tests, the TCE was completely degraded faster than expected (one of them is shown in Fig. 4). In the others, the time required to degrade approximately 70–90% of the initial mass of TCE was shorter than predicted, but the time to completely degrade the TCE was longer than predicted (Fig. 5).

Observed and predicted degradation behaviors were compared based on initial degradation rates and $t_{0.99}$, the time to remove 99% of the initial mass of TCE (Table 2). The initial rate of degradation was calculated by performing a linear regression on the first few observed and predicted data points. Enough data points were included in each regression to yield a coefficient of determination (R^2) value close to 0.95. The mass of microcapsules varied among the batch tests, so the initial degradation rate was normalized by the initial mass of KMnO_4 present, in units of μmol of TCE degraded per mg of KMnO_4 initially present per day. The $t_{0.99}$ values were calculated by linear interpolation of the last few data points.

The results show that the average initial degradation rate was approximately three times faster, and the average $t_{0.99}$ was three times longer than predicted using the permanganate release data (Table 2). The data are variable, however, so the populations of predicted and observed values were compared using a Student's t -test to determine if they were drawn from different populations (McClave and Dietrich 1991). The results confirm the observations that most of the initial degradation rates were drawn from separate populations ($\alpha=0.05$). The exceptions were for samples 19-307 and 19-308. The results for the $t_{0.99}$ values were less straightforward. The predicted and observed values of $t_{0.99}$ for three samples (19-307, 19-308, and 19-550) were statistically significant, but not for the others.

These results suggest that the diffusive release of KMnO_4 and the stoichiometric degradation of TCE are unable to account for the details of the TCE degradation process. It appears that some processes other than simple release occur during TCE degradation. Additional experiments were performed to provide insights into those other processes.

Trichloroethene Adsorption and Mass Balances

The extent of ICE adsorption was examined with samples of 19-363, Boler wax, and Chlorez 700. Fitting the data to the Freundlich isotherm [Eq. (10)] yielded reasonably consistent $1/n$ values, ranging from 1.03 to 1.12. However, values for K_f varied

widely, from a low of 0.045 for Boler wax to 2.05 (L mg^{-1}) (mg g^{-1}) for Chlorez 700 (Table 3). To place these results in context, Freundlich isotherm coefficients for adsorption of ICE to granular activated carbon are $K_f=28$ (L mg^{-1}) (mg g^{-1}) and $1/n=0.62$ (Snoeyink 1990). At $C_e=92$ mg L^{-1} , the q_e for Chlorez 700 is approximately 70% of the value for activated carbon, versus only 1.0 and 3.0% for Boler wax and sample 19-363, respectively. Chlorez 700 is a chlorinated wax that was selected because it was expected that TCE might strongly partition into this compound.

Mass balances were conducted by measuring the concentrations of permanganate, chloride, and potassium, and then comparing the results to the mass of TCE that was degraded at the time the samples were taken. MnO_4^- concentrations were measured during tests with samples 19-546, 19-548, 19-550, and 19-553, and they were negligible in each case. The concentrations of MnO_4^- at the end of the tests (85 d) were expected to range from 113 to 395 μmol per bottle, based on the difference between $C_{r,\text{max}}$ and the stoichiometric amount of KMnO_4 needed to oxidize the initial mass of ICE in each test. The measured MnO_4^- concentrations were only 0.46 (± 0.73) and 0.23 (± 0.40) μmol per bottle in two samples, and were undetectable in the others.

The concentration of K^+ was measured several times during tests with samples 19-546, 19-548, 19-550, and 19-553. The reaction stoichiometry indicates 2.0 mol of K^+ released per mol of TCE degraded. The average ratio was 1.88 (± 0.20), ranging from 1.61 to 2.44. These results indicate that 80–122% of the expected K^+ was in solution.

Chloride concentrations were measured at the end of the tests with samples 19-546 through 19-553. The reaction stoichiometry indicates 3.0 mol Cl^- released per mol of TCE. The average ratio was 2.56 (± 0.05), ranging from 2.50 to 2.64. These results indicate that 85% of the Cl^- produced by TCE degradation was accounted for.

The mass balance results indicate that there is a sink for

Table 3. Freundlich Parameters for Trichloroethene (22–24°C)

Sample	$1/n$	K (L mg^{-1}) (mg g^{-1})
19-363	1.029	0.133
Boler wax	1.014	0.0448
Chlorez 700	1.121	2.05
Activated carbon	0.62	28

permanganate and chloride other than in the solution. The magnitude of this sink, as judged by the deviation from the stoichiometric ratio, differs among the ions: it is a strong sink for permanganate and a weak sink for chloride. The data also suggest a weak sink for potassium, but those results are inconclusive due to a high degree of variability.

Discussion

The large differences among permanganate release rates are apparently due in part to the process used to fabricate the microcapsules. The relatively fast release of material from the SGC samples can be explained by observations made under a reflected-light microscope. Microcapsules were sliced with a razor to reveal the structure of the core and shell. SGC samples typically contained cores of single grains of KMnO_4 . The shell material was asymmetrically distributed around the core grains, so the core was either exposed or covered by an extremely thin layer of shell. Many of the SGC microcapsules were somewhat elongated, with core grains exposed at one end of the long axis. It seemed reasonable to expect that the fast release was occurring where the core was exposed at the edge of the microcapsule. This was confirmed by placing individual microcapsules in a drop of water and observing under the microscope. Vivid purple plumes of permanganate always emanated where core grains were exposed at the edges of microcapsules.

It appears that during the microencapsulation process, the molten shell material flowed away from the leading edge and toward the leeward side after each SGC particle was shed from the spinning disk. The shell solidified in this distribution, exposing the core material at one location. The rotation rate of the disk was slowed when the MGC material was made. This produced somewhat larger droplets containing between 10 and 20 grains, and microscopic examination revealed that, in general, the grains were uniformly distributed within the capsules. None of the grains appeared to be exposed at the surface of observed MGC microcapsules, and only slight wisps of purple permanganate were noted when individual capsules were observed in water droplets under the microscope.

Other variations in the release rate appear to result from the chemical composition of microcapsules. Microcapsules 19-549 and 19-553 released permanganate for the longest times (Table 1). They contain the highest concentrations of Chlorez 700. The other two samples containing Chlorez 700 (19-550 and 19-551) also had relatively long release times. The most rapid release among the MGC samples occurred with 19-306, which is the only sample to contain Epolene C-10.

Final concentration ratios, $C_{r,\max}$, of the samples were expected to be 1.0, but the average value was 0.88 (± 0.09) for SGC and MGC samples. This suggests approximately 10% of the expected mass of permanganate was somewhere other than in solution. Three possible explanations are (1) some KMnO_4 remained in the microspheres after release appeared to be complete; (2) the amount of KMnO_4 in the microspheres was overestimated; and (3) some KMnO_4 was consumed by oxidation of the shell material or by autodecomposition.

The experiments show that microcapsules will release KMnO_4 over several weeks and that they can effectively degrade TCE. The rate of degradation is generally similar to that expected based on the rate of release of permanganate, but there are some important differences between the predicted and observed degradation rates. The initial rate of degradation is three to four times faster

than the predicted rate, and observed $t_{0.99}$ values were either similar to, or longer than, predicted. In addition, concentrations of certain daughter products of the degradation reaction (chloride and permanganate) were less than expected based on the stoichiometry [Eq. (1)].

MnO_4^- and MnO_2 were both identified visually in solution during the degradation of TCE, indicating that some permanganate had diffused out of the microcapsules and was reacting with TCE in solution. In addition, TCE can partition to shell material and it can strongly partition to the shell material containing chlorinated wax. It seems likely that TCE will diffuse into the shell material, and it follows that TCE diffusing into the microcapsules could react with permanganate diffusing outward from the core. This could cause deposition of $\text{MnO}_2(s)$ within the shell matrix pores, which could in turn change the effective diffusion of both reactants.

TCE adsorbing onto, or diffusing into, the microcapsules is one explanation for the initial rate of reaction occurring faster than expected. In addition, the chemical potential gradient driving diffusion out of the microcapsules was probably steepened by the degradation of permanganate reacting with TCE in a boundary layer on the outer surface of the microcapsules. TCE degrading in the boundary layer would have increased the rate that permanganate was released compared to the control.

The process of inward diffusion of TCE could account for compounds missing from the mass balance. TCE that reacted with permanganate within the shell would create daughter products (e.g., chloride, potassium, MnO_2) within the shell where they would be isolated from water analyses. The degradation reaction would slow as a consequence of an increase in the concentration of daughter products, so an accumulation of daughter products is one explanation for the decrease in degradation rate observed in many of the tests.

These results suggest that it may be feasible to design a microcapsule that releases permanganate to solution extremely slowly (e.g., by increasing shell thickness) using a shell material that has a strong affinity for chlorinated compounds. TCE that adsorbs or dissolves into the shell material would be degraded internally by the permanganate it contains. One advantage of this approach is that it could isolate permanganate from nonchlorinated organic compounds in solution. This would allow the permanganate to selectively target dissolved chlorinated compounds and avoid being consumed by oxidizing harmless natural organic material.

The results of this study demonstrate that it is feasible to encapsulate KMnO_4 in a polymer and create compounds that have the potential for useful environmental applications. The ability to release permanganate over more than 2 months seems to be particularly suited to processes in remote locations where injecting a permanganate solution with a metering pump is infeasible. Microencapsulation essentially eliminates readily soluble permanganate and fine permanganate dust. This makes the microcapsules safer to handle than raw permanganate, especially because there appears to be no inhalation hazard associated with the microcapsules. Guar gum gel, which is commonly employed to suspend particulates used to fill reactive barriers (Murdoch et al. 1997), is rapidly degraded by raw permanganate. However, when we placed MGC microcapsules in cross-linked guar gel, the slurry maintained a high viscosity and shear strength for at least several hours. It therefore appears that the microcapsules could be suspended in a slurry of guar gum gel and injected to create permeable reactive barriers in the subsurface.

The microcapsules tested for this work would be suited to

creating permeable reactive layers in the subsurface however, other applications may benefit from smaller microcapsules. For example, microcapsules that are small enough to enter pores could be dispersed in a porous material to degrade contaminants far from the point of injection. A variety of encapsulation methods are available for future investigations to create microcapsules with a wide range of sizes and properties.

Conclusions

Samples of KMnO_4 were encapsulated in waxy polymers and used in batch tests to evaluate their potential for slowly releasing permanganate and for degrading TCE in solution. The samples released permanganate for an average of 27 days, ranging from 3 to 80 days. The average final concentration ratio, $C_{f, \text{max}}$, was $0.88 (\pm 0.095)$ (g KMnO_4 released/g KMnO_4 initial⁻¹), ranging from 0.80 to 1.05 g KMnO_4 released/g KMnO_4 initial⁻¹. The initial rate of release was roughly constant, but it decreased with time and was effectively modeled using a simple function with two empirical parameters [Eq. (7)]. These results demonstrate that it is feasible to design microcapsules that release permanganate over predictable schedules for a wide range of periods (from a few days to a few months).

TCE was degraded to less than detectable amounts in the presence of the KMnO_4 microcapsules. In batch TCE tests, the average initial degradation rate was $1.8 (\pm 0.15)$ ($\mu\text{mol TCE d}^{-1} \text{mg KMnO}_4^{-1}$), ranging from 0.07 to 3.8 $\mu\text{mol TCE d}^{-1} \text{mg KMnO}_4^{-1}$. The average $t_{0.99}$ value for all MGC microcapsules was $15.5 (\pm 5.2)$ days, ranging from 1.3 to 30.9 days.

The rate of TCE degradation was predicted using the observed release history of KMnO_4 and assuming an ideal reaction stoichiometry. In general, these predictions were reasonable, but there were some systematic errors. The observed rates of TCE degradation were generally three to four times faster than the predicted rates during the first few days of the tests. TCE was completely removed in some tests after a few days. However, where TCE was present for longer than a few days, the degradation reaction rate decreased and was less than predicted based on the release rate.

It is clear that TCE is degraded by permanganate diffusing out of the microcapsules, but it also appears that TCE diffuses into and is degraded within some microcapsules, particularly where chlorinated polymer is used as a shell. As a result, some daughter products of the degradation reaction might remain trapped within the microcapsule, so analysis of the water alone would fail to close a mass balance. Moreover, the accumulation of daughter products could limit diffusion of aqueous species between the core and the shell. If this occurred, it would slow the degradation reaction and could account for the slow rates at the end of some tests.

The degradation of TCE that potentially diffuses into microcapsules is particularly significant because it provides a mechanism for creating materials that selectively oxidize some organic compounds while leaving others unaffected. TCE strongly adsorbed to one of the chlorinated waxes used as a shell material. It therefore seems feasible to use this type of shell material to selectively degrade dissolved chlorinated compounds and exclude natural organic material associated with subsurface solids. Metals mobilization could potentially be minimized if oxidation occurs inside the microcapsules.

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