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Production and Characterization of Encapsulated Potassium Permanganate for Sustained Release as an in Situ Oxidant

Namgoo Kang, Inez Hua,* and P. Suresh C. Rao

School of Civil Engineering, Purdue University, 1284 Civil Engineering Building Rm 3145E, 550 Stadium Mall Drive, West Lafayette, Indiana 47907-1284

Potassium permanganate (KMnO_4) has been widely applied as an oxidant for in situ remediation of contaminated groundwater and soil. This study describes the creation and characterization of encapsulated KMnO_4 particles, the purpose of which is to serve as a material that can be specifically targeted and delivered to a contaminant source zone for optimal oxidative destruction of the contaminant. Multinuclear particulate KMnO_4 with a mean equivalent spherical diameter of $15 (\pm 8.6) \mu\text{m}$ was incorporated into a paraffin wax matrix and then pulverized, resulting in completely or partially encapsulated particles with a mean equivalent spherical diameter of $874 (\pm 377) \mu\text{m}$. Paraffin wax is biodegradable and insoluble in water, and yet is very soluble in most hydrophobic contaminants, including chlorinated solvents such as perchloroethylene (PCE). Thus, KMnO_4 is released very slowly into water from the encapsulating matrix, but the oxidant is rapidly released into PCE. The release kinetics of KMnO_4 from the encapsulated particles into water were characterized by an initial rapid release (<10 min), followed by significantly sustained release in later stages. The estimated times for 90% release of the oxidant were 1.6 months, 19.3 years, and 472 years for paraffin wax to KMnO_4 mass ratios of 1:1, 2:1 and 5:1, respectively. The encapsulated KMnO_4 particles preferentially accumulated at the PCE-water interface, and the KMnO_4 was rapidly released into pure phase PCE (~ 3 min) as the paraffin wax completely dissolved.

Introduction

Controlled release techniques have attracted attention in diverse fields such as pharmaceutical and agrochemical technologies.^{1–3} However, controlled release of an oxidant into a subsurface environment is an emerging concept relevant to environmental engineering. In particular, the controlled release of oxidants during the application of in situ oxidation merits investigation.

In situ chemical oxidation (ISCO) of chlorinated dense nonaqueous phase liquids (DNAPLs) by potassium permanganate (KMnO_4) has been described in numerous reports.^{4–7} Excess oxidant is often required for rapid destruction because of nonspecific oxidant losses; this is true regardless of the type of oxidant. For example, it has been reported that the mass ratio of KMnO_4 to trichloroethylene (TCE, 1.0 L) was 82:1 to achieve complete destruction within 120 days during a 3-D flow tank study.⁴ Another example is that the mass ratio of KMnO_4 to perchloroethylene (PCE, 0.576 L) was 73:1 to destroy $\sim 41\%$ of the total mass of DNAPL over 63 days in a 1-D column experiment.⁶ Because the oxidant also reacts with natural organic matter, inorganic soil constituents, and other reduced compounds, only a small fraction of the applied oxidant actually reaches and

attacks the target compound. Therefore, it is advantageous to develop delivery methods that minimize non-specific oxidant losses, and thereby decrease the amount of oxidant needed for a particular cleanup.

The remediation performance of ISCO strongly depends on how KMnO_4 is delivered into the contaminated zone. Currently, delivery system configurations include pressurized direct-push or augured probe permeation, soil mixing, hydraulic fracturing, vertical or horizontal well flushing, treatment walls, and oxidant recirculation.^{8–10} However, few studies on controlled (sustained) oxidant delivery systems have been conducted, particularly for KMnO_4 .^{10–12} One report documents solid oxidant particle mixtures (OPMs) with a grain size of less than ~ 5 mm containing KMnO_4 granules suspended in clay or cement plus water as a carrier fluid.¹¹ The OPMs are proposed for use in a treatment zone approach; once they are introduced into the subsurface soil and groundwater, they would release the oxidant slowly (over a period of months to years). The oxidant would migrate by molecular diffusion or advection and react with the contaminant.¹¹ However, there are other possible approaches to the controlled release of KMnO_4 .

Especially for source zone remediation, controlled release of KMnO_4 may be achieved by completely or partially coating the water-soluble solid KMnO_4 with a water-insoluble matrix. The purpose of the coating would be to prevent contact between the aqueous

* To whom correspondence should be addressed. Tel.: (765) 494-2409. Fax: (765) 496-1988. E-mail: hua@purdue.edu.

solution (groundwater) and the oxidant and thus control the dissolution rate of KMnO_4 before the oxidant reaches the targeted contaminant.⁹ A coating material should therefore possess several essential characteristics. The material should be a solid at ambient temperature, water insoluble, soluble in the target organic contaminant, chemically compatible and mutually immiscible with KMnO_4 , and environmentally benign.

The first objective of the present study was to generate and characterize encapsulated KMnO_4 particles potentially applicable to the oxidation of hydrophobic organic contaminants in groundwater and soil. A further objective was to probe the release characteristics from the coated KMnO_4 particles into aqueous solutions and an organic contaminant, which, in this case, was PCE. Commercially available paraffin wax was selected as a coating material and matrix for particulate KMnO_4 .

Experimental Methods

Materials. KMnO_4 (particle size, -325 US mesh; purity, 97%) was purchased from Aldrich. Paraffin wax with a melting (congealing) range of 50–55 °C was obtained from Fluka. Reagent grade water was prepared from distilled water purified by reverse osmosis and a Barnstead NANOpure II deionizing system ($\Omega = 18.0 \text{ M}\Omega/\text{cm}$).

Particle Size Reduction. The particle sizes of uncoated KMnO_4 particles (UPPs) or encapsulated KMnO_4 granules (EPGs) were reduced by processing each material with a laboratory mill (IKA A1 Basic Mill). The working principle of this mill is based on impact milling and the process type is batch. Preliminary tests revealed that continuous high-speed rotation (a maximum of 28 000 rpm when unloaded) of the stainless steel blade raised the temperature sufficiently such that particle agglomeration occurred. To minimize this agglomeration, a stepwise milling process was employed; each step included power-on (milling) for 5 min and a subsequent power-off (>6 h) until the mill temperature returned to ambient. Because milling performance leveled off after 20 min, UPPs were milled for 20 min to produce uncoated, milled KMnO_4 (UMPPs) which were then employed as the core material for encapsulation.

Encapsulation. A molten suspension and cooling (MSC) method, modified from a melt-dispersion technique^{13,14} was employed for the encapsulation of KMnO_4 (the oxidant) with a paraffin wax as the coating material (matrix). Solid paraffin wax (10.0 g) was introduced into a 100-mL Pyrex beaker, which was placed on a hot plate-sitter (Cimarec top stirring hotplate). The temperature of the wax was maintained at 80–85 °C and it was stirred at 300 rpm with a glass magnetic bar (2.0 cm). UMPPs (2–10 g) were gradually added to the molten wax while continuously mixing (15 min) to ensure uniform dispersion of the KMnO_4 in the wax phase. Approximately 0.5 mL of the molten suspension was rapidly transferred into reagent grade water. The molten suspension drops solidified into encapsulated KMnO_4 granules (EPGs). The EPGs were collected after vacuum filtration and desiccation for 24 h. The encapsulated KMnO_4 particles (EPPs) were generated by pulverizing the EPGs in the laboratory mill for 3 min.

Microscopic Evaluation. The shape and surface characteristics of the UPPs, UMPPs, and EPPs were observed using visual imaging instruments. An optical

microscope (AxioCam optical microscope system, Zeiss), a scanning electron microscope (SEM, JSM-35CF, JEOL), and an environmental SEM (ESEM, system 2020, ElectroScan) were utilized to gather information on the particles during various stages of processing.

Particle Size Analysis. Particle size distribution and mean particle sizes were determined using a laser light diffraction particle size analyzer (Beckman Coulter LS 230) equipped with a Small-Volume Module Plus and Coulter LS Particle Characterization software version 2.11a. Approximately 0.15 g of the test material was introduced into the sample vessel containing ~20 mL of toluene (for UPPs) or isopropyl alcohol (for EPPs) as the suspension fluids. To prevent agglomeration, the sample was sonicated in a water bath (Branson 5210) at 45 W for 5 min. The suspension fluid and dispersed particles flowed through the sample cell and hoses in a closed-loop system. Light passed through a diffraction sample cell during measurement. The obscuration level (extent of attenuation of incident beam intensity due to the presence of particles)¹⁵ was calculated to be nearly 45%. The Fraunhofer diffraction solution was employed as the optical model for particle size estimation because it is applicable when particles are coarser than ~2 μm and because it is independent of any properties (e.g., refractive index) of the particles being tested.¹⁵ The particle size distribution results were expressed as a function of the equivalent spherical diameter on a volume basis. The equivalent spherical diameter is defined as the diameter of a regular, homogeneous sphere that has the same volume as the particle being measured and represents three-dimensional properties of the real particle.¹⁵

Thermal Analysis. Thermal properties of selected samples were measured with differential scanning calorimetry (DSC 2920 System, TA Instruments). The purge gas was nitrogen (flow rate 35 mL/min). The initial temperature was 20 °C and ramped at 10 °C/min to 140 °C. Aluminum sample pans were utilized.

Determination of Mass Recovery. An extraction procedure was employed to determine the actual mass of KMnO_4 within the paraffin wax matrix and the mass recovery of KMnO_4 loaded in the EPPs. The EPPs (0.20 g) were introduced into a 25-mL volumetric flask containing 20 mL of cyclohexane. The flask was tightly capped, vortexed, and placed on a rotary wheel shaker for 24 h to ensure complete dissolution of the paraffin wax. The suspension was transferred to a 1.0-L volumetric flask and reagent grade water was added to extract the KMnO_4 . The aqueous and organic phases were vigorously mixed for 1 h and maintained in contact for another 1 h, after which the organic and aqueous phases were separated. The concentration of permanganate ion in the aqueous phase was determined by measuring the absorption at $\lambda = 552 \text{ nm}$ with a UV-Visible spectrophotometer (Perkin-Elmer Lambda 3) and by measuring the manganese (Mn) content with an atomic absorption spectrophotometer (AAS, Varian SpectrAA-20 Plus) equipped with a graphite tube atomizer (Varian GTA-96). The molar absorptivity, λ_{552} , for permanganate ion was $2221 \text{ M}^{-1} \text{ cm}^{-1}$.

Release Experiments. The EPPs (0.30, 0.15, and 0.10 g for the mass ratios of 5:1, 2:1, and 1:1 paraffin wax/ KMnO_4 (W/P), respectively) were introduced into 1.0 L of reagent grade water at room temperature under constant mixing (200 rpm) with a mechanical stirrer (Arrow 6000) to ensure a well-mixed solution. With

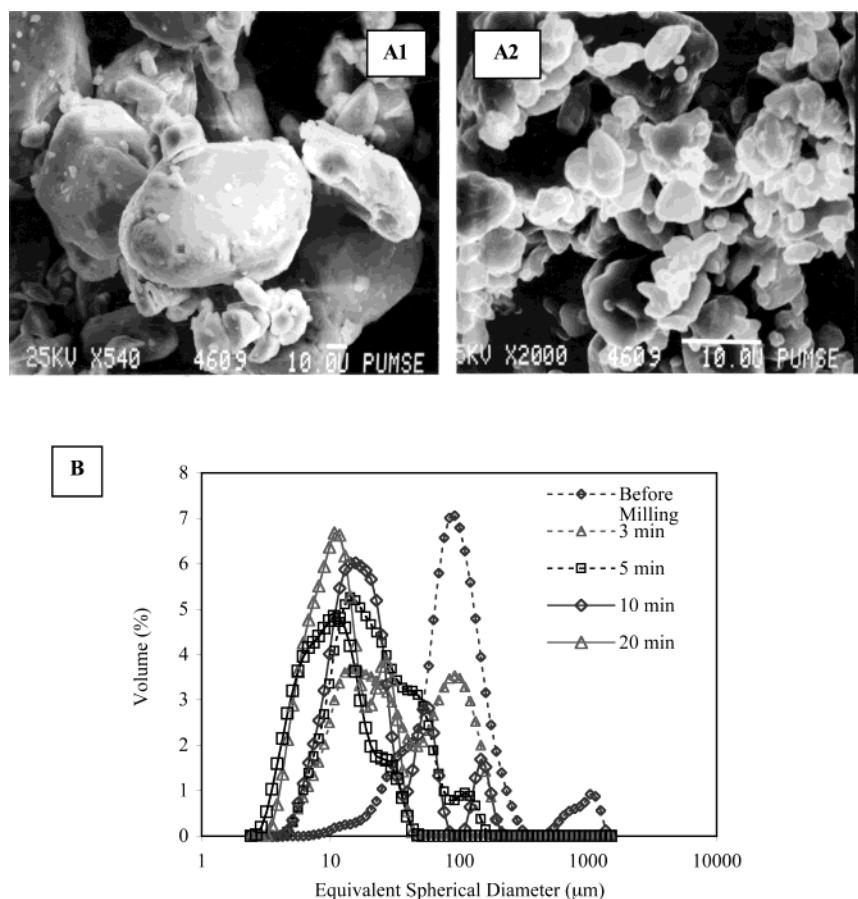


Figure 1. Characterization of uncoated KMnO_4 particles: (A1) SEM image before milling (scale bar, $10\ \mu\text{m}$); (A2) SEM image after milling for 20 min (scale bar, $10\ \mu\text{m}$); (B) particle size reduction as a function of milling time.

special care to prevent the uptake of the particles, samples (4.0 mL) of the aqueous solution were withdrawn at 1, 2, 3, 4, 5, 10, 20, 30, 60, 120, 800, and 1200 min using a glass syringe (Micro-mate Interchangeable) equipped with a stainless steel needle (30 cm long). The samples were transferred to 7-mL glass vials. In a separate set of experiments, the EPPs were also introduced into pure PCE to confirm that the paraffin wax coating would rapidly dissolve when in contact with the target contaminant. EPPs (0.10 g) of varying W/P ratios were introduced into pure PCE (5 mL) and agitated for 1 min on an orbit shaker at 200 rpm at room temperature.

The concentration of permanganate ion in the aqueous phase was determined by measuring the absorption at $\lambda = 552\ \text{nm}$ with a UV-Visible spectrophotometer (Perkin-Elmer Lambda 3). The release of KMnO_4 from the UMPPs (milled for 20 min) into reagent grade water was also measured as the control experiment.

Results and Discussion

Both elemental and UV-Vis spectrophotometric analyses confirmed that the recovery of KMnO_4 in the aqueous solution after dissolution of the paraffin wax coating (i.e., encapsulation efficiency) approached 100%.

SEM images and the size distribution of UPPs are presented in Figure 1. UPPs are characterized by sharp edges and very irregular shapes including elliptical or bar-type with varying size distribution. The comparison of the two images from before and after milling suggests that milling resulted in significant size reduction of

UPPs. Particle size distribution analyses demonstrate that mean particle size (\pm standard deviation) decreased from $152 (\pm 222)$ to $15 (\pm 9)\ \mu\text{m}$ after milling for 20 min. However, it was observed from both SEM (Figure 1A) and the particle size distribution (Figure 1B) that particles much smaller than the mean diameter were present in each batch.

Encapsulated KMnO_4 granules (EPGs) with a size of 0.5–5 mm were milled to produce smaller particles (Figure 2). ESEM images demonstrate that multinuclear, micronized KMnO_4 particles were randomly entrapped in the paraffin wax matrix.

The particle distribution of EPPs for 2:1 W/P followed a bimodal curve with a mean diameter of $874 (\pm 377)\ \mu\text{m}$. The particle size distribution curve was obtained in duplicate. It was observed that the distributions were relatively reproducible regardless of random sampling of the powder as well as varying speeds (50, 60, and 70% of the maximum circulation speed) in the loop system of the module used in this study. As a quantitative measure, the sum of standard deviations from all the data points of the duplicate samples was 17.2% (as volume %) relative to 100% of total volume.

Figure 2B suggests that some of the EPPs formed aggregates. The paraffin wax matrix is very cohesive, resulting in the second peak at a particle diameter of $1700\ \mu\text{m}$. EPPs with a higher mass fraction of KMnO_4 (50% for 1:1 W/P) contained more KMnO_4 particles embedded on the surface and thus a rougher surface than those with a lower mass fraction of KMnO_4 (33.3% for 2:1 W/P). There was no significant difference in the mean diameter for different mass ratios of W/P.

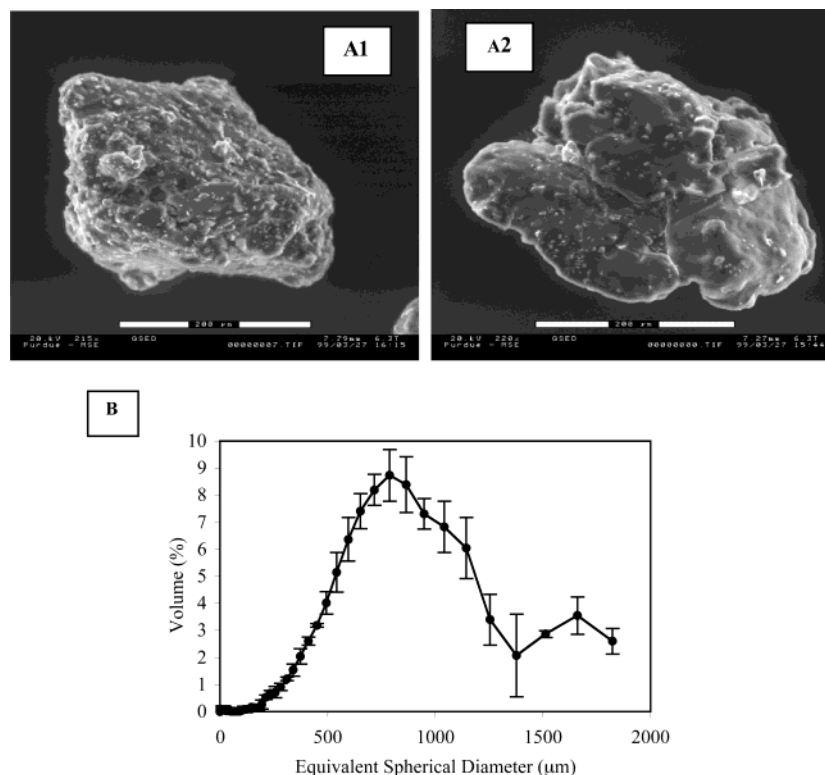


Figure 2. Pulverized encapsulated KMnO_4 particles: ESEM images (scale bar, 200 μm) for 1:1 W/P (A1) and 2:1 W/P (A2); (B) particle size distribution of duplicate samples as volume percent for 2:1 W/P.

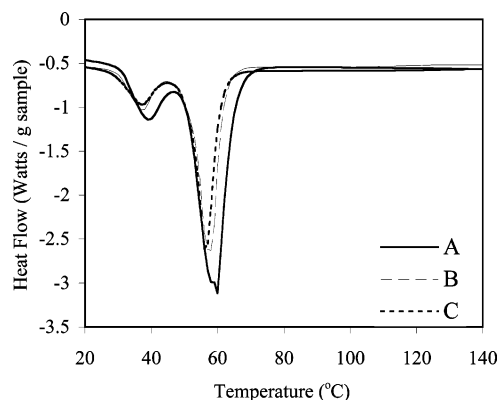


Figure 3. Differential scanning thermograms: (A) paraffin wax; (B) physical mixture of paraffin wax and uncoated KMnO_4 particles; and (C) encapsulated KMnO_4 particles (1:1 W/P).

DSC data indicate the melting behavior of the paraffin wax before and after the modified MSC process. KMnO_4 particles and paraffin wax are inert toward each other over a range of temperatures (Figure 3). Endothermic peaks in a differential scanning thermogram usually represent melting temperatures and energy of the tested materials. Because most paraffin waxes retain residual oil ($\sim 0.5\%$), paraffin waxes usually do not exhibit sharp melting points.¹⁶ The two characteristic melting ranges with the smaller peak at 30–50 $^{\circ}\text{C}$ and the bigger one at 50–70 $^{\circ}\text{C}$ were observed for the paraffin wax. There was no significant difference between melting ranges of the wax in the presence and in the absence of KMnO_4 particles and no additional peaks were detected. It is therefore likely that the solid KMnO_4 particles do not significantly interact with the paraffin wax over the temperature range in which the MSC process was conducted. These results are consistent with previous reports that significant oxidation of

paraffin wax exposed to oxidants does not occur until the temperature reaches 93 $^{\circ}\text{C}$ and requires at least 3 days at 121 $^{\circ}\text{C}$.¹⁶ The paraffin wax, therefore, will not contribute to nonspecific losses of the KMnO_4 during delivery and transport of the particles.

Figure 4 shows release profiles of KMnO_4 from EPPs into reagent grade water. Dissolution of the UPPs was immediate (<1 min), whereas that of the EPPs was significantly retarded: 10–45% of the KMnO_4 was released in 4 days. The release of the oxidant from the particles into reagent grade water was biphasic and characterized by an initial rapid release (<10 min) followed by a significantly sustained release. The initial fast release is due to dissolution of uncoated or incompletely coated KMnO_4 particles which are embedded into or near the surface of the EPPs and which are readily accessible to water. The depletion of KMnO_4 at the surface of the particles is shown in Figure 5. After 4 days of continuous contact with reagent grade water, empty crevices appeared on the surface of the paraffin wax medium.

These results are in good agreement with previous findings that a highly water soluble core material such as potassium chloride exhibits biphasic release patterns.¹⁷ The rapidly stirred reactors represent very turbulent conditions, and therefore the measured release rates into water should be considered an upper limit. The release rates of the EPPs may be slower under less turbulent flow conditions such as ground-water flow.

To elucidate release mechanism, several models, including zero-order kinetics, the Sinclair and Peppas equation,¹⁸ modified first-order kinetics,¹⁹ and a modified hyperbola model,²⁰ were tested to fit to the experimental data sets. Among them, the simplified empirical equation (eq 1) proposed by Sinclair and Peppas could best simulate ($r^2 > 0.974$) the release kinetics for the

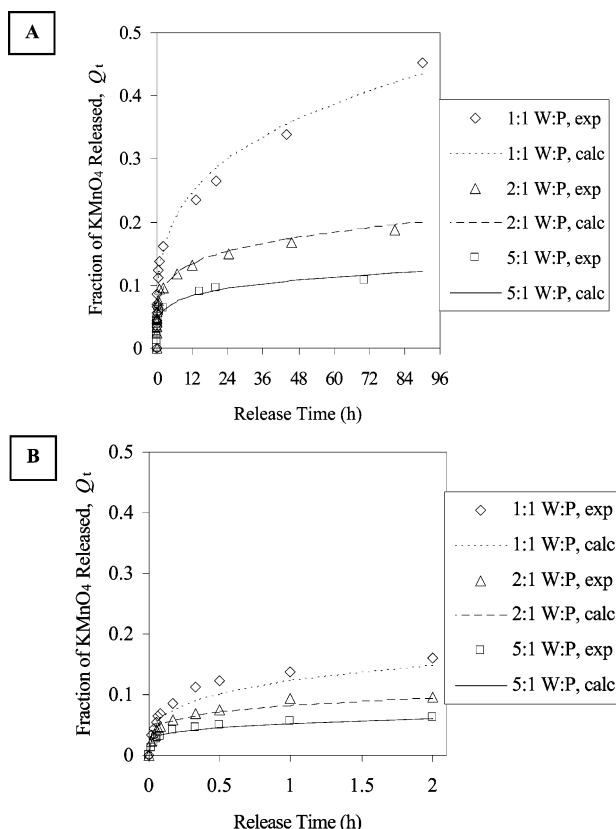


Figure 4. Experimental data and calculated values (eq 1) for KMnO₄ released over time from the paraffin wax matrix into reagent grade water: (A) overall plots; (B) data points near $t = 0$.

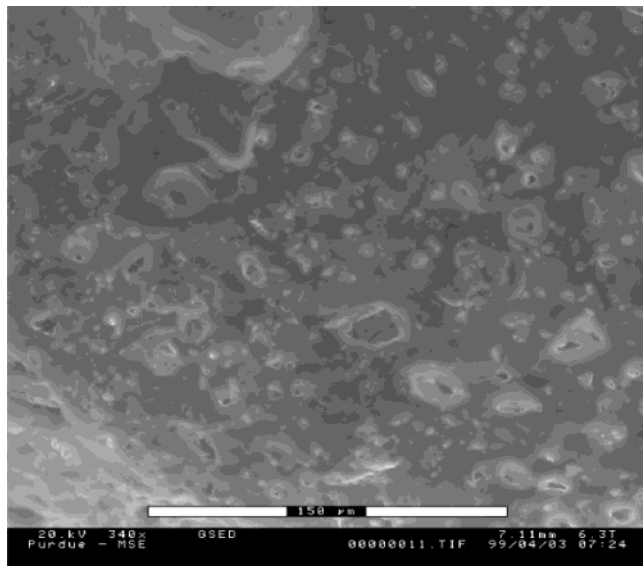


Figure 5. ESEM image of the surface of an encapsulated KMnO₄ particle (1:1 W/P; scale bar, 150 μm) after 4 days of stirring in reagent grade water. Note crevices which remain after the KMnO₄ has dissolved in the water.

experimental data sets while curve-fitting results were not as good ($r^2 < 0.900$) with the other models.

$$Q = kt^n \quad (1)$$

where Q is the fraction of the active agent (KMnO₄) released at time t , k is a constant incorporating the characteristics of the active agent and matrix (paraffin wax) system and has units of t^{-n} , and n is the diffusional

Table 1. Estimated Values of the Model Parameters Fitted to Experimental Data Sets for Release Tests in Reagent Grade Water

paraffin wax/KMnO ₄ (by mass)	r^2	n	$k (t^{-n})$	SSE	$t_{0.9}$
1:1	0.987	0.282	0.122	5.04×10^{-3}	1.7 mo
2:1	0.974	0.200	0.081	1.64×10^{-3}	19.3 yr
5:1	0.993	0.187	0.052	1.7×10^{-4}	472 yr

exponent. This equation suggests that the release process is non-Fickian diffusion with constant pseudo-convection due to the stress within the wax matrix.¹⁸ The rapid dissolution of KMnO₄ particles on the wax surface leaves crevices and pores. It is hypothesized that these pores may possibly generate inter-particulate openings or channels within the wax matrix. Consequently, the aqueous phase may diffuse in and contact the remaining KMnO₄ in the matrix.

The values of n and k are usually obtained by linearizing eq 1 in logarithmic form (eq 2), plotting experimental data, and determining the slope and the intercept on the axis of $\log Q$, respectively.

$$\log Q_t = \log k + n \log t \quad (2)$$

However, it has been documented that even if the square of the correlation coefficient for the fitting of experimental data to a linearized model (eq 2) is acceptable (e.g., $r^2 = 0.99$), the estimated values may not necessarily simulate nonlinear release kinetics with accuracy.¹⁸ For this reason, the parameters were estimated in this study by an optimization method which minimizes the sum of the square of errors (SSE) between the experimental (after 5 min) and the calculated data.

$$SSE = \sum_t (Q_{t,\text{exp}} - Q_{t,\text{calc}})^2 \quad (3)$$

Accordingly, the time required for 90% release of the oxidant ($Q = 0.9$), $t_{0.9}$, can be estimated using the following:

$$t_{0.9} = \left(\frac{0.9}{k} \right)^{1/n} \quad (4)$$

For the EPPs with varying ratios of W/P, Table 1 presents the estimated values of r^2 obtained from eq 2, n , k , and SSE from eq 3, and $t_{0.9}$ from eq 4. Table 1 indicates that the model fits were in good agreement with the experimental data sets, suggesting that the model could adequately describe the release kinetics of KMnO₄ from the wax matrix. The estimated values of n (0.187, 0.200, and 0.282) were consistent with a reported range (0.173 to 0.261) obtained from eq 2 fitted to release data sets of various fertilizers (monoammonium phosphate and diammonium phosphate) from a paraffin wax in deionized water in the absence of stirring.²⁰ This comparison suggests that, in the later stages, release characteristics from paraffin wax matrices would be similar regardless of system agitation.

The model prediction results indicate that time scale for 90% release ranged from over a month (1.7 months for 1:1 W/P) to years (19.3 and 471 yrs for 2:1 and 5:1 W/P, respectively). This estimation clearly suggests that the fraction of KMnO₄ completely sequestered in the wax matrix is almost completely inaccessible to water, and that permeation (diffusion) of water into the wax matrix should be sufficiently slow.

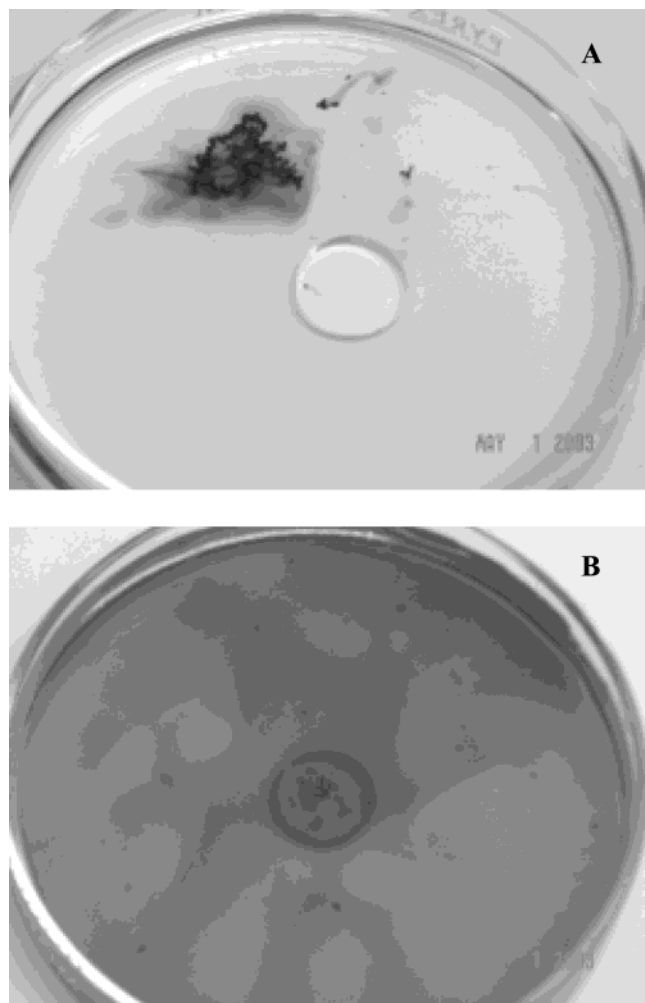


Figure 6. Accumulation of pulverized encapsulated KMnO_4 particles (0.05 g, 2:1 W/P) at the surface of a PCE droplet (0.7 mL) in reagent grade water: (A) before agitation; (B) 10 min after the system was agitated for 1 min.

A primary factor governing KMnO_4 release in the examined system may be the ratio of W/P. The results from Figure 4 and Table 1 clearly indicate that the mass fraction of KMnO_4 released into water at a given time is closely related to the mass fraction of UPPs utilized in the modified MSC process. The release rate is proportional to the mass fraction of UPPs and inversely proportional to the mass fraction of the paraffin wax.

Selected experiments were conducted to examine the dissolution of the paraffin wax coating in PCE, a representative dense nonaqueous phase liquid (DNAPL). Not surprisingly, encapsulated KMnO_4 particles with a higher mass fraction of the paraffin wax (83 wt %; 5:1 W/P) dissolved more slowly than those with paraffin mass fractions of 66.7 wt % (2:1 W/P) and 50 wt % (1:1 W/P). However, for the three ratios of W/P, complete dissolution of the paraffin wax coating occurred within 3 min of contact with PCE. Rapid release of the oxidant from the encapsulation matrix is an essential aspect of targeted delivery. Because the paraffin wax coating readily dissolves in PCE, it is reasonable to expect that if the EPPs were to contact the contaminant phase, KMnO_4 would be released at an enhanced rate.

Figure 6 demonstrates how the EPPs behave in the presence of PCE droplets in reagent grade water before and after the suspension is agitated. The EPPs prefer-

Table 2. Solubility of Paraffin Wax (Melting Point of 51.4–53 °C) in Various Organic Solvents^a

solvent	solubility at 20 °C (g/mL)
carbon tetrachloride	0.317
benzene	0.285
chloroform	0.246
tetrachloroethylene (PCE)	~0.20 (22 °C) ^b
hexane	0.0831
cyclohexane	0.0776 (16.7 °C)
TCE	0.0286 (15 °C)

^a From ref 16. ^b Measured value in this work.

entially agglomerate at the interface of the free-phase PCE due to the affinity of the paraffin wax for PCE. The fact that the EPPs collected at the interface of free-phase PCE and water represents a local enhancement of oxidant concentration relative to the bulk solution.

The paraffin wax used as the matrix material for solid KMnO_4 particles meets the criteria for a suitable coating material. Paraffin wax is a solid at room temperature and consists mostly (80–90% w/w) of straight chain hydrocarbons (20–30 carbon atoms per chain).¹⁶ Paraffin wax is also soluble in many organic contaminants including chlorinated compounds (e.g., TCE and PCE) as summarized in Table 2.¹⁶ However, it is practically insoluble in water.^{16,22} Saturated hydrocarbons, such as paraffin waxes, are relatively inert to KMnO_4 oxidation. Finally, paraffin wax is fully biodegradable.^{23,24} For example, hydrocarbon-oxidizing bacteria including *Pseudomonas*, *Mycobacterium*, *Nocardia*, *Corynebacterium*, and *Micrococcus* are known to degrade petroleum fractions rich in paraffin (>80%).²³ It has been documented that nearly 60% and 40% of initial mass of linear and branched paraffin waxes were biodegraded over three months in a soil system.²⁴

Conclusions

Paraffin wax was applied as an environmentally benign and inert matrix for protecting solid KMnO_4 particles from rapid dissolution and undesirable reactions in moist conditions. Multinuclear EPGs with a size range of about 0.5–5 mm were generated using a modified MSC process. The release of KMnO_4 from the EPPs into reagent grade water was characterized by a relatively fast initial rate followed by a significantly slower rate in the later phase, and release of KMnO_4 into pure phase PCE was almost instantaneous. Consequently if the EPPs directly contact separate phase contaminant, the contaminant will be subjected to locally high concentrations of KMnO_4 released into the aqueous phase adjacent to the contaminant.

The modified MSC method has many advantages over other encapsulation techniques because it does not require specialized equipment and it is easily scaled up to produce larger quantities of particles. Furthermore, the method does not require organic solvents, and the encapsulation efficiency of KMnO_4 is approximately 90%. However, there are some potential limitations to the particles, as currently produced. A fundamental requirement for in situ transport of particles is that their size be less than the smallest radius of the pores in which substantive advective flow occurs. The coated particles described in this article are almost a millimeter in average radius, whereas particles occupying the lower end of the size distribution would be more useful. Thus, technological improvements are needed to generate

smaller particles. A further improvement would be to reduce the amount of KMnO_4 that dissolves into water during the initial stage of release, by enhancing the paraffin coating on KMnO_4 grains that are embedded at the surface of the encapsulated particles. In addition to the limitations due to large size of the EPPs, there may be other uncertainties as to their contact with residual separate phase contaminants in porous media. Factors which determine the extent of contact include (i) physical and chemical properties of the EPPs (e.g., density, extremely hydrophobic coating); (ii) characteristics of the porous media (e.g., pore sizes and organic-rich mineral surfaces); and (iii) hydrodynamic conditions (e.g., flow rates).

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