



Stabilization of potassium permanganate particles with manganese dioxide

Klara Rusevova, Frank-Dieter Kopinke, Anett Georgi*

UFZ, Helmholtz Centre for Environmental Research, Department of Environmental Engineering, Permoserstrasse 15, 04318 Leipzig, Germany

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ABSTRACT

A new potassium permanganate reagent with slow-release properties was designed and tested for possible application in *in situ* chemical oxidation. For this purpose, MnO₂-coated KMnO₄ particles (MCP) were prepared by partial reduction of solid KMnO₄ using the acid-catalyzed reaction with n-propanol or the comproportionation of Mn(VII) and Mn(II) in n-propanol as reaction medium. Column tests showed that, for MCP with a residual KMnO₄ fraction of 70 wt%, the duration of permanganate release under flow-through conditions was prolonged by a factor of 10 compared to untreated KMnO₄. While KMnO₄ is too soluble to be used in reactive barriers, MCP could be introduced into the aquifer by filling of trenches or boreholes; this would allow a prolonged passive dosing of permanganate into the flowing groundwater. In addition, experiments were conducted in order to determine the oxidation capability of native KMnO₄ particles and MCP in CH₂Cl₂, a representative non-polar non-aqueous phase liquid (NAPL). It may be possible to utilize the significantly higher reactivity of MCP under these conditions for the design of slow-release permanganate particles for NAPL source treatment.

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1. Introduction

Potassium permanganate (KMnO₄) has been widely used for the treatment of pollutants in drinking water and wastewater for over 50 yr. At the end of the last century, KMnO₄ also became widely used as an oxidant for *in situ* chemical oxidation (ISCO) (Siegrist et al., 2001), providing a rapid and cost-effective treatment technique for non-aqueous phase liquid (NAPL) source zones, or zones of high residual contamination.

KMnO₄, which is usually injected into the contaminated zone as an aqueous solution, is in many cases able to transform the contaminants into products that are harmless to the environment. The half-life or longevity of KMnO₄ depends on site-specific conditions (Huling and Pivetz, 2006). There are several problems associated with ISCO by permanganate. The first problem is non-target permanganate consumption – called Natural Oxidant Demand (NOD), in which permanganate, as a non-specific oxidant, reacts with natural organic matter and other naturally occurring species that can be oxidized (Urynowicz, 2008). Therefore, only a small fraction of the applied oxidant actually reaches and attacks the contaminant. The second problem is associated with the difficulty of controlling the distribution of permanganate in the subsurface. Non-uniform distribution of the oxidant can cause incomplete contaminant degradation. In many cases, source-zone treatment is not adequate for reaching remediation goals (regulatory limits), and treatment of the contaminated groundwater plume must also be

implemented. A third problem is the formation of MnO₂ coatings on the surface of the NAPL phase during ISCO with dissolved KMnO₄, inhibiting further access to the oxidant (MacKinnon and Thomson, 2002; Crimi and Siegrist, 2004).

Permeable reactive barriers (PRBs) have gained significant attention as a remedial technology due to their favorable cost/benefit ratio and the potential of PRBs for reducing the spread of contaminants (Gavaskar, 1999). PRBs are constructed in the subsurface such that they intercept a contaminant plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms in order to attain remediation concentration goals down-gradient of the barrier (Gavaskar et al., 2002). The most widely known solid barrier for passive remediation is zero-valent iron, which is used in reactive barriers for the reduction of halogenated hydrocarbons (for instance, to convert trichloroethene (TCE) into ethene and ethane). To the best of our knowledge, no solid barrier is being used for passive oxidative remediation at the moment, with the exception of oxygen-releasing compounds (ORCs) (Koenigsberg and Sandefur, 1999) which are used for *in situ* bioremediation. KMnO₄ is unsuitable for this technique due to its high solubility in water and subsequent mobility in groundwater, but a delivery system with a slow release of permanganate might overcome these obstacles. Two types of approaches for slow-release of permanganate have been proposed: (I) a delivery system consisting of KMnO₄ granules dispersed in an inert organic crystalline matrix for placement in wells (Lee and Schwartz, 2007; Lee et al., 2008) and (II) the preparation of single KMnO₄ particles stabilized by organic coatings (Kang et al., 2004; Ross et al., 2005). KMnO₄ encapsulated by paraffin wax has been

* Corresponding author. Tel.: +49 341 235 1760; fax: +49 341 235 1471.
 E-mail address: anett.georgi@ufz.de (A. Georgi).

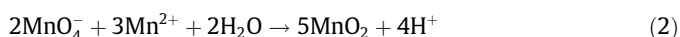
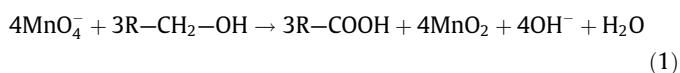
proposed as a specifically-targeted oxidant for optimal *in situ* destruction of the contaminant with decreased NOD (Kang et al., 2004). Based on the finding that the paraffin wax dissolves rapidly in a perchloroethylene phase, the encapsulation approach was suggested for treatment of NAPL contaminations. Another work focused on the encapsulation of permanganate in various waxy polymers and studied the oxidant release properties of the respective microcapsules together with the degradation of TCE in water (Ross et al., 2005). The authors suggested that degradation of TCE is based not only on diffusion of permanganate into the water phase, but possibly also on the diffusion of TCE into the microcapsules, where it reacts with permanganate (Ross et al., 2005).

Permanganate particles with increased life time, especially those with hydrophobic coating, might be able to enter into NAPL phases. Thus the reaction medium would change from water (as in application of dissolved permanganate) towards a non-aqueous medium. The reactivity of aqueous permanganate towards many substrates is widely documented (Waldemer and Tratnyek, 2006), whereas its reactivity in more or less non-polar phases has not been so thoroughly investigated.

The objective of our study was to develop stabilized permanganate particles with slow-release properties, and possibly improved oxidation efficiencies in media other than water, which could enlarge the potential applications of permanganate oxidation processes for *in situ* remediation. In the first part of our paper, the reactivity of KMnO_4 in a non-polar solvent as a model situation for NAPLs is studied. KMnO_4 is known to be highly reactive in water. However, in organic synthesis, special procedures are applied in order to conduct oxidation reactions with permanganate in non-aqueous media. This includes application of organic-soluble permanganate salts, such as tetraethylammonium permanganate (Dash et al., 2009), or application of KMnO_4 on solid supports. Immobilization of KMnO_4 on the surface of solid supports such as aluminum silicate, hydrated alumina or active MnO_2 can lead to modifications in its chemical reactivity and selectivity (Shaabani and Lee, 2001; Shaabani et al., 2004; Dash et al., 2009).

The second part of our paper focuses on a novel way of encapsulating KMnO_4 particles. A promising coating material for KMnO_4 particles with controlled-release properties could be manganese dioxide (MnO_2). Manganese dioxide is insoluble in water and organic solvents, and can act as adsorbent and catalyst (Hammel et al., 2002). MnO_2 also has further desirable properties: it can be prepared by low-cost procedures and is considered as environmentally harmless (Greenwood and Earnshaw, 1997). In the literature, the combination of KMnO_4 and active MnO_2 has been described as an effective oxidant for a variety of organic compounds under solvent-free and heterogeneous conditions (Shaabani et al., 2004).

In our experiments, we tried to synthesize MnO_2 -coated KMnO_4 particles (MCP) directly by partial reduction of KMnO_4 microparticles. Two different reaction pathways were tested: (I) reduction of KMnO_4 by primary alcohols (Eq. (1)), and (II) redox reaction between Mn^{2+} and MnO_4^- (Eq. (2)). The oxidation of primary alcohols in water is well-known in organic chemistry and leads to carboxylic acids as final products, whereby KMnO_4 is reduced to MnO_2 . On the other hand, the reaction between Mn^{2+} and MnO_4^- is a known disproportionation reaction (Ma et al., 2006).



It is the basic idea of our approach, that the permanganate reduction takes place as heterogeneous reaction and that the formed MnO_2 adheres directly at the surface of the KMnO_4

particles. Primary alcohols, which cause only minor dissolution of KMnO_4 , were used as reaction medium for both reactions and as reducing agent in reaction I.

2. Experimental part

2.1. Materials

All of the chemicals used in the following experiments: potassium permanganate, n-propanol, manganese(II) nitrate tetrahydrate, benzene, dichloromethane, benzaldehyde and H_2SO_4 (98%), were purchased from Merck (Germany) or Sigma-Aldrich (Germany) and had a purity of $\geq 99\%$. KMnO_4 was sieved to a size fraction of 63–250 μm .

2.2. Experimental Methods

2.2.1. Solvent effect on oxidation with KMnO_4

Benzaldehyde was chosen as a model reactant for evaluating the influence of the reaction medium on the oxidation with potassium permanganate. Batch experiments were performed at ambient conditions ($23 \pm 2^\circ\text{C}$) using glass vials with screw caps and Teflon-coated septa. Vials were shaken during the experiment on a horizontal shaker. The oxidation of benzaldehyde (10 mg) with KMnO_4 (0.5 g) was tested in three different systems: (I) in 10 mL dichloromethane without the presence of water, (II) in 10 mL dichloromethane which contained 0.5% v/v dissolved H_2O , and (III) in a two-liquid-phase system consisting of 1 mL of water and 9 mL of dichloromethane. Benzene, (10 mg) which has a very low reactivity with permanganate (Waldemer and Tratnyek, 2006), was used as an inert internal standard in all three systems. Benzene, benzaldehyde and the product of oxidation, benzoic acid, were analyzed in aliquots of the dichloromethane phase by means of GC-MS (Agilent) in the selected ion monitoring mode. Samples were analyzed after 3 h reaction time and then after every 24 h for 4 d.

2.2.2. Preparation of MnO_2 -coated KMnO_4 particles

The coating of KMnO_4 with MnO_2 was performed in batch experiments, carried out in 50 mL glass flasks placed on a heating plate with magnetic stirring. During the reaction, the temperature was kept at 90°C . KMnO_4 was treated according to the following procedures (R_0 , R_1 or R_2), all with n-propanol as reaction medium. For reactions R_0 and R_1 , 0.5 g KMnO_4 was suspended in 15 mL n-propanol. In the case of reaction R_1 , additionally 100 μL H_2SO_4 (50%) was added as catalyst. For reaction R_2 , 0.1 g $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 15 mL n-propanol, to which 0.5 g KMnO_4 particles were then added. Reaction times of 0.5, 1, 2 and 3 h were applied for each of the three procedures.

The coated permanganate particles obtained were filtered, air dried and further investigated.

2.2.3. KMnO_4 release and recovery tests

The dissolution of KMnO_4 from MCP and the amount of residual KMnO_4 after the treatment were determined in a column experiment. A glass column (ID = 0.3 cm, l = 10 cm) was filled with a homogenous mixture of 0.3 g quartz sand (grain size $\leq 250 \mu\text{m}$) and 0.1 g MCP or native KMnO_4 particles, for comparison under dry conditions. The filled column (bed height = 4.5 cm, bed volume = 0.32 cm^3 , porosity = 0.35) was flushed with CO_2 in order to accelerate the saturation of the column packing after starting the water flow. The water used for experiments was de-gassed by purging with helium. In the column experiment, water was pumped through the column in the upwards direction using a piston pump. The water flow rate was 0.7 mL min^{-1} . The kinetics of

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