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THE EFFICIENT DETERMINATION OF RATE CONSTANTS FOR OXIDATIONS BY PERMANGANATE

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ABSTRACT: An efficient protocol for measuring oxidation rates of many contaminants by permanganate has been developed using time-resolved spectrometry at an absorbance maximum of permanganate (525 nm). The contaminants of concern were used in excess to maintain pseudo-first-order conditions. Because the colloidal manganese dioxide that forms from oxidations by permanganate also absorbs at 525 nm, we developed a procedure that uses both permanganate and manganese dioxide absorbance to calculate pseudo-first-order rate constants. Second-order rate constants were determined from pseudo-first-order rate constants obtained at several initial concentrations of contaminant. The second-order rate constants obtained with our method are in good agreement with previously reported values, and we are now focusing on contaminants for which kinetic data are not currently available.

INTRODUCTION

When determining the feasibility of in situ chemical oxidation (ISCO) for treatment of a contaminated site, knowledge of the oxidation rates of the contaminants to be treated is critical. Although permanganate has become a popular oxidant for ISCO, the only contaminant class for which there is extensive rate data is the chlorinated ethylenes. Unfortunately, there are very few data on the rate at which permanganate oxidizes important contaminants of other chemical classes (such as BTEX, oxygenates, explosives, and phenols). A protocol that enables the efficient determination of rate constants for these contaminants is needed.

UV spectroscopy is a convenient way to measure permanganate oxidation rates. Permanganate absorbs strongly at 525 nm; therefore, we can use low concentrations of permanganate and maintain pseudo-first-order conditions even with contaminants that are only moderately water-soluble. Unlike gas chromatography, UV spectroscopy does not require the development of new methods for analyzing chemicals of different chemical classes. This allows rate constants for the oxidation of many contaminants to be determined efficiently.

EXPERIMENTAL METHOD

Chlorinated ethylenes were obtained in high purity from Sigma-Aldrich and used to make saturated solutions (1 ml of a chlorinated ethylene was added to 20 ml of water, shaken vigorously, and allowed to equilibrate overnight). Pseudo-first-order conditions were maintained by using at least a 10:1 ratio of contaminant to permanganate. A UV/VIS spectrophotometer (Perkin-Elmer model Lambda 20) was used to measure decreasing absorbance at 525 nm, an absorption maximum for permanganate. A 50 mM phosphate buffer was used to keep the pH constant at 6.5 and to inhibit flocculation of the colloidal particles of manganese dioxide (Mata-Perez and Perez-Benito, 1985).

Two experimental methods, which we call *stopped-flow* and *static*, were used to analyze the chlorinated ethylenes. Advantages of the static method are that it is simple and gives less run-to-run variability. However, many fast-reacting contaminants have half-lives less than the ~30 seconds required to set up the static method—these are the contaminants that we analyzed by the stopped-flow method. Figure 1 shows the method best suited to different chlorinated ethylenes.

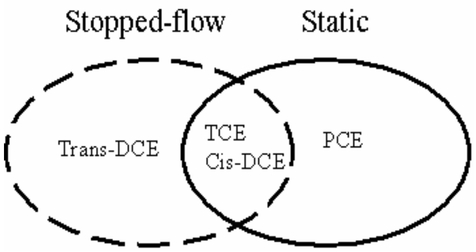

FIGURE 1. The stopped-flow method is used to measure fast oxidation reactions, such as trans-dichloroethylene (trans-DCE). The static method is used to measure slower oxidation reactions, such as perchloroethylene (PCE). The reactions of permanganate with trichloroethylene (TCE) and cis-dichloroethylene (cis-DCE) have rates that are suitable for measurement by either method.

The static method involves premixing the permanganate and the chlorinated ethylene in a 5 ml quartz cuvette. As mentioned above, this method is used for slow reactions (reactions that take 60 minutes or longer to reach completion). The stopped-flow apparatus consists of two gas-tight syringes (one for the permanganate and one for the chlorinated ethylene stock solution) that are connected to a mixing cell (2 µl dead volume) that leads to a quartz flow-through cuvette (path-length 1 cm). A syringe pump enables quick delivery (~1 sec) from the mixing cell to the cuvette. Second-order rate constants were determined from the slope of the regression line fit to pseudo-first-order rate constants of reactions for different contaminant concentrations. As shown in Figure 2, comparable results are obtained with the two methods for TCE.

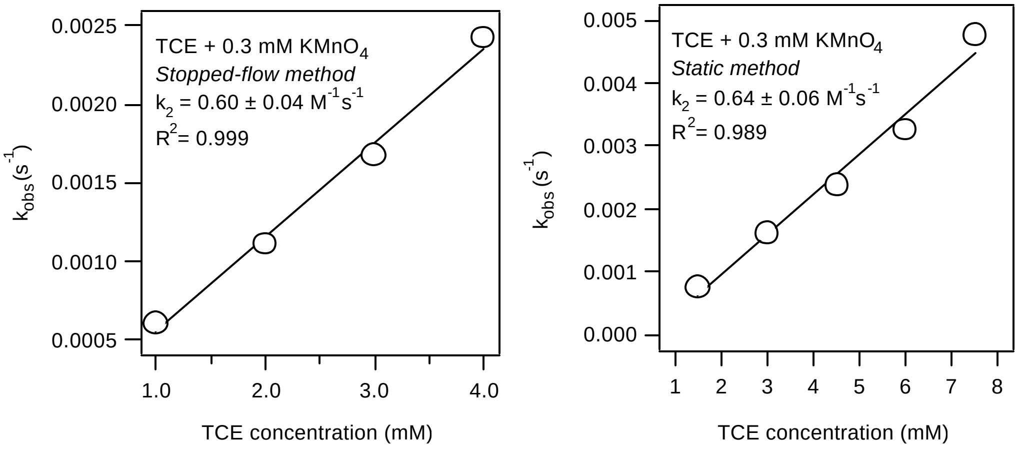

FIGURE 2. Stopped-flow and static methods give similar second-order rate constants for permanganate oxidation of TCE.

DATA ANALYSIS

It has been shown by others that the product of permanganate oxidation is colloidal manganese dioxide, which absorbs at 525 nm (Lee and Perez-Benito, 1985; Mata-Perez and Perez-Benito, 1985; Perez-Benito and Arias, 1992; Gardner, 1996; Yan and Schwartz, 1999). However, as long as a sharp isosbestic point is maintained during successive scans of the reaction, Beer's Law holds and light scattering can be neglected. A linear relationship between the absorbance at 525 nm (where both permanganate and manganese dioxide absorb) and the absorbance at 418 nm (where only manganese dioxide absorbs) provides additional evidence that Beer's Law holds (Mata-Perez and Perez-Benito, 1985; Perez-Benito and Arias, 1992). Figures 3A and 3B show both methods of verifying Beer's Law using data from the same experiment. For reactions that were too fast to be measured with successive scans, a sharp isosbestic point could not be used to verify that Beer's Law was obeyed. Instead, we ran replicate experiments, monitoring one at 525 nm and the other at 418 nm—a linear relationship between the two was used to verify that Beer's Law was obeyed (data not shown).

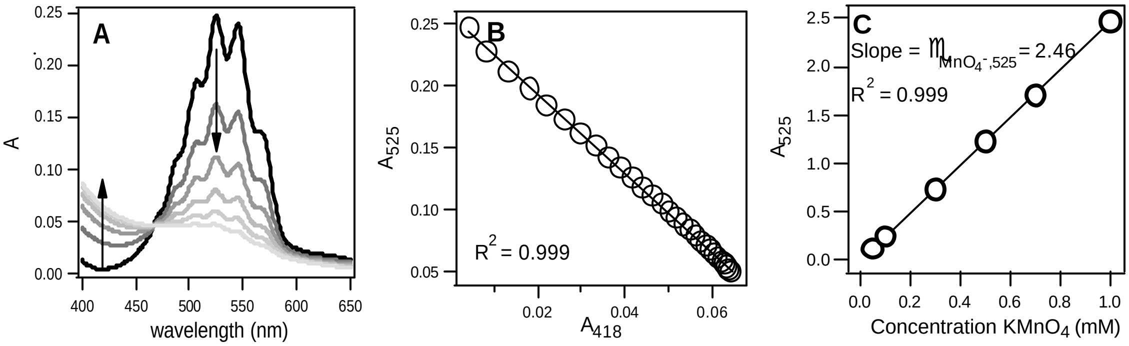

FIGURE 3. A) Successive scans (in 12 minute intervals) of the reaction between 0.1 mM permanganate and 1.0 mM TCE. Absorbance decreases at 525 nm and increases at 418 nm as the permanganate is depleted by reaction with TCE and manganese dioxide is produced. Note the sharp isosbestic point at 467 nm. B) A linear relationship between the 525 nm vs. 418 nm data used to create Figure 3A provides additional verification that manganese dioxide follows Beer's Law. C) Determination of $e_{MnO_4^-,525}$ by measuring A_{525} at different concentrations of permanganate.

Assuming that permanganate and manganese dioxide are the only species absorbing light at 525 nm, Beer's Law states that for any point in the reaction:

$$A_{525} = [MnO_4^-]*e_{MnO_4^-,525} + [MnO_2]*e_{MnO_2,525} \qquad [1]$$

where $e_{MnO_4^-,525}$ and $e_{MnO_2,525}$ are the absorptivities of permanganate and manganese dioxide at 525 nm. While $e_{MnO_4^-,525}$ can be determined from the slope of an absorbance vs. concentration plot (see Figure 3C), the colloidal nature of the manganese dioxide makes it difficult to determine either the concentration of manganese dioxide or $e_{MnO_2,525}$.

In addition to showing when Beer's Law is obeyed, a sharp isosbestic point also implies that no long-lived intermediates are formed during the reaction (Lee and Perez-

Benito, 1985). Therefore, the total concentration (C_t) of permanganate and manganese dioxide must be equal to the initial amount of permanganate used:

$$C_t = [MnO_4^-]_o = [MnO_4^-] + [MnO_2] \qquad [2]$$

Mechanistic studies of the chlorinated solvents (PCE, TCE, cis-DCE, and trans-DCE), toluene, and MTBE have been shown to be first order with regard to both contaminant and permanganate (Gardner, 1996; Yan and Schwartz, 1999; Huang et al., 2001; Damm et al., 2002). As these contaminants represent several different chemical classes, it seems reasonable to assume that permanganate will follow first-order degradation kinetics with most contaminants. Because manganese dioxide is the only species that absorbs at 418 nm, this assumption can be verified by fitting a first-order appearance curve to the manganese dioxide absorbance data (Figure 4A). Using the assumption of first-order degradation kinetics, Equation 1 can be rewritten as:

$$A_{525} = [C_t e^{-k_{obs}*t}]*e_{MnO_4^-,525} + [C_t - C_t e^{-k_{obs}*t}]*e_{MnO_2,525} \qquad [3]$$

where k_{obs} is the pseudo-first-order rate constant. Equation 3 can be applied to the A_{525} vs. time data to obtain fitted values for both k_{obs} and $e_{MnO_2,525}$. Chi-squared values for data fitted with Equation 3 are smaller than 0.001 (Figure 4B). The k_{obs} values obtained from Equation 3 were used to determine second-order rate constants (Figure 2) and the order of reaction with respect to the contaminant of concern (Figure 4C).

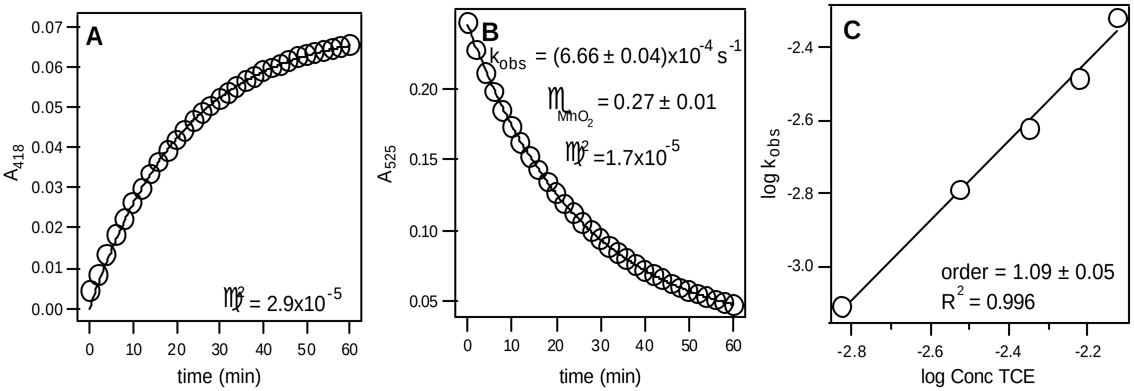

FIGURE 4. A) Example of a first-order appearance curve fit to A_{418} vs. time data. B) Example of A_{525} vs. time data fit with equation 3 for the reaction of 1 mM TCE and 0.1 mM permanganate. C) Determination of order of reaction with respect to TCE using the static method.

COMPARISON OF RESULTS

Although k_{obs} and $e_{MnO_2,525}$ are fit simultaneously, both parameters have standard deviations of less than 10% in most cases (Figure 4B), indicating that the uncertainty associated with these fitted values is small. The second-order rate constant for the oxidation of TCE by permanganate obtained by this method is comparable to previously published rate constants (Table 1). This method needs no modification to analyze compounds of different chemical classes, making it easy to efficiently analyze a wide range of compounds. We are currently applying this method to representative contaminants in the classes of explosives, phenols, oxygenates, chlorinated methanes, and BTEX.

TABLE 1. Comparison of 2nd-order rate constants for the oxidation of TCE by permanganate.

Reference	k_2 $M^{-1}s^{-1}$	[TCE] (mM)	[$KMnO_4$] (mM)	pH	Temp (°C)
Huang et al., 2001	0.80	0.10 - 0.19	1.6 - 6.3	7	20
Hunkeler et al., 2003	0.77				
Poulson and Naraoka, 2002	0.55	0.38 -1.9	0.32	Not buffered	23
Siegrist et al., 2001	0.89			6.9	20
Vella and Veronda, 1993	0.68	0.19 - 0.38	0.051-0.063	6.25	
Yan and Schwartz, 1999	0.66	0.078	0.37 - 1.2	7.1	
This study	**0.64**	**1.5 - 7.5**	**0.3**	**6.5**	**25**

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REFERENCES

Damm, J.H., C. Hardacre, R.M. Kalin, and K.P. Walsh. 2002. "Kinetics of the oxidation of methyl tert-butyl ether (MTBE) by potassium permanganate." *Water Research*. *36*(14): 3638-3646.

Gardner, K.A. 1996. "Permanganate Oxidations of Aromatic Hydrocarbons in Aqueous and Organic Solution." Ph.D. Thesis, University of Washington, Seattle, Washington.

Huang, K.C., G.E. Hoag, P. Chheda, B.A. Woody, and G.M. Dobbs. 2001. "Oxidation of chlorinated ethenes by potassium permanganate: a kinetics study." *Journal of Hazardous Materials*. *87*(1-3): 155-169.

Hunkeler, D., R. Aravena, B.L. Parker, J.A. Cherry, and X. Diao. 2003. "Monitoring oxidation of chlorinated ethenes by permanganate in groundwater using stable isotopes: Laboratory and field studies." *Environmental Science and Technology*. *37*(4): 798-804.

Lee, D.G., and J.F. Perez-Benito. 1985. "Oxidation of hydrocarbons. 14. Autocatalysis during the oxidation of 1-tetradecene by methyltributylammonium permanganate." *Canadian Journal of Chemistry*. *63*(6): 1275-1279.

Mata-Perez, F., and J.F. Perez-Benito. 1985. "Identification of the product from the reduction of permanganate ion by trimethylamine in aqueous phosphate buffers." *Canadian Journal of Chemistry*. *63*(4): 988-992.

Perez-Benito, J.F., and C. Arias. 1992. “Occurrence of colloidal manganese dioxide in permanganate reactions.” *Journal of Colloid and Interface Science*. *152*(1): 70-84.

Poulson, S.R., and H. Naraoka. 2002. “Carbon isotope fractionation during permanganate oxidation of chlorinated ethylenes (cDCE, TCE, PCE).” *Environmental Science and Technology*. *36*(15): 3270-3274.

Siegrist, R.L., M.A. Urynowicz, O.R. West, M.L. Crimi, and K.S. Lowe. 2001. *Principles and Practices of In Situ Chemical Oxidation Using Permanganate.* Batelle Press, Columbus, OH.

Vella, P.A., and B. Veronda. 1993. *Oxidation of trichloroethylene: A comparison of potassium permanganate and Fenton's reagent*. 3rd International Symposium, Chemical Oxidation: Technology for the Nineties, Vanderbilt University, Nashville, TN, 17-19 February 1993. Technomic, Lancaster, UK. *3*: 62-78.

Yan, Y.E., and F.W. Schwartz. 1999. “Oxidative degradation and kinetics of chlorinated ethylenes by potassium permanganate.” *Journal of Contaminant Hydrology*. *37*(3-4): 343-365.