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Applications of Potassium Permanganate in the Oxidative Degradation of Trichloroethylene

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Abstract

The scope of this study was to determine techniques to remediate trichloroethylene contamination under different environmental conditions, media and in co-existence with chromium. The specific objectives were focused on the oxidation of trichloroethylene (TCE) in soil and aqueous media using both unmodified $KMnO_4$ particles and poly (methyl methacrylate), PMMA encapsulated $KMnO_4$ in the presence and absence of hexavalent chromium, Cr(VI). Molar ratios (p-values) of $KMnO_4$ to TCE were used as a determining factor in the TCE oxidation process. p-values of 2, 5 and 10 were investigated in aqueous media and an approximately 0.5 $M^{-1} \cdot s^{-1}$ rate constant was obtained using unmodified $KMnO_4$ in aqueous system. The extent of oxidation did not change with TCE concentration. In soil system, TCE oxidation requires a large amount of $KMnO_4$ to produce similar results as in aqueous system. pH experiments indicate that except at high alkaline condition, pH does not impact the extent of TCE oxidation. Also, the presence of Cr(VI) did not hinder TCE oxidation by $KMnO_4$. Using controlled release application, the rate of TCE oxidation was reduced by PMMA encapsulated $KMnO_4$. Comparative study indicated an expectedly slow rate of TCE degradation using modified $KMnO_4$ but similar overall extent of oxidation for both modified and unmodified $KMnO_4$. The application of the encapsulated matrix yielded 88% ± 3% TCE oxidation and a simultaneous 81% ± 2.1% Cr(VI) reduction by ferrous ion in the same system.

Keywords

Trichloroethylene, Kinetics, Permanganate, Oxidation, Poly Methyl Methacrylate, Mixed Contaminants

1. Introduction

Chlorinated hydrocarbon in groundwater, soil and sludge is of global concern due to its high toxicity, stability
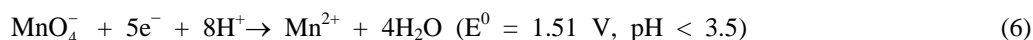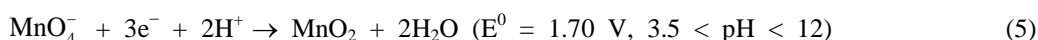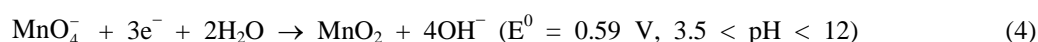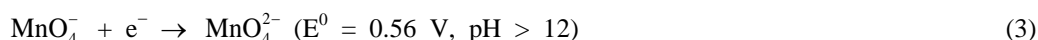
and widespread applications. *In-situ* chemical oxidation (ISCO) has been successfully used to degrade chlorinated hydrocarbons for decades [1] [2]. One of the popularly applied oxidants in ISCO is $KMnO_4$ which may be due to its high oxidation potential across the pH meter [3]. Contaminants come in different species in hazardous waste sites. The mutual presence of organic and inorganic contaminants on several DOE sites is a complex problem in the design of degradation process. The co-existence of heavy metals and chlorinated hydrocarbon is common in most hazardous waste sites as included in the EPA National Priority List (NPL) (HazDat, 2007). A study by Joeng and Hayes in 2007 indicated that the rates and pathways of dechlorination of chlorinated hydrocarbons using other reducing agents were very well influenced by the presence of heavy metals [4].

Furthermore, oxidation of TCE and Cr(VI) by an oxidizing agent is by analogy the oxidation of TCE in the presence of Cr(VI); research has shown that TCE is dichlorinated in the presence of Fe(II) [5]. Therefore, combining the above two processes simultaneously could result in some undesirable products (e.g. vinyl chloride and Cr(VI)). In the oxidation of TCE by permanganate in the presence of Cr(VI), there are perhaps two parallel reactions that can be proposed as described by Equations (1) and (2) below. However, the likely conversion in 2 is very low about 0.05% in soil [6].

$$C_2HCl_3 + 2KMnO_4 \rightarrow 2MnO_2 + 3Cl^- + H^+ + 2CO_2 \text{ (g)} + 2K^+ \tag{1}$$

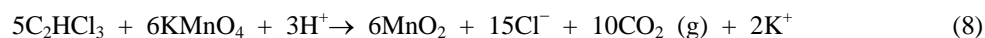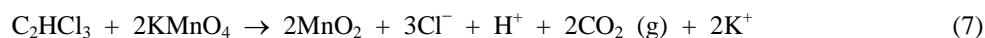$$3MnO_2 + 4Cr(III) \rightarrow 4Cr(VI) + 3Mn + 2O_2 \tag{2}$$

Huang *et al.* (2000) in a study indicated that while remediating dissolved-phase TCE could be rapid by introducing the appropriate oxidant, degradation of source zone (pure TCE) was very slow. This was explained as due to the slow mass transfer between the oxidant in aqueous phase and the pure TCE phase at the interface [7]. Thus the use of potassium permanganate with a high aqueous solubility of 64 g/L at 20°C in TCE source zone (aqueous solubility of TCE is 1.28 mg/L) would be much difficult. As a strong and reactive oxidant, $KMnO_4$ would oxidize any reductive organic material dissolved in an aqueous medium. Hence the amount of $KMnO_4$ available to oxidize the target contaminant is reduced thereby decreasing the oxidation efficiency. More $KMnO_4$ than necessary is therefore used for complete degradation of the target compound [8]. Therefore, the availability of $KMnO_4$ in aqueous phase can be controlled by slowing down its dissolution rate through encapsulation.

Permanganate is effective in ethylene oxidation because it is selective towards the double bond (functional group, C=C) [9]. Permanganate application in *in-situ* chemical oxidation of trichloroethylene results in Cl^-, CO_2, H^+, and MnO_2 or Mn^{2+}. The Mn^{2+} is further oxidized to form MnO_2 [10]. The formation of MnO_2 or Mn^{2+} is a function of pH conditions of the system. According to Equations (3)-(6), the relative high oxidation potential of $KMnO_4$ varies at different pH ranges.

$$MnO_4^- + e^- \rightarrow MnO_4^{2-} \text{ } (E^0 = 0.56 \text{ V, pH} > 12) \tag{3}$$

$$MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 + 4OH^- \text{ } (E^0 = 0.59 \text{ V, } 3.5 < \text{pH} < 12) \tag{4}$$

$$MnO_4^- + 3e^- + 2H^+ \rightarrow MnO_2 + 2H_2O \text{ } (E^0 = 1.70 \text{ V, } 3.5 < \text{pH} < 12) \tag{5}$$

$$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O \text{ } (E^0 = 1.51 \text{ V, pH} < 3.5) \tag{6}$$

Due to the different oxidation potential exhibited at different pH values, the pathway for TCE oxidation would vary (see **Figure 3**). Several intermediates are produced in this reaction. However, the final product remains that CO_2 is produced [11]. Thus, the reaction between TCE and $KMnO_4$ is very complex since it involves multiple intermediate steps and alternate pathways depending on pH of media. The overall reaction has been compressed into the forms in Equations (7) and (8) [11]-[13].

$$C_2HCl_3 + 2KMnO_4 \rightarrow 2MnO_2 + 3Cl^- + H^+ + 2CO_2 \text{ (g)} + 2K^+ \tag{7}$$

$$5C_2HCl_3 + 6KMnO_4 + 3H^+ \rightarrow 6MnO_2 + 15Cl^- + 10CO_2 \text{ (g)} + 2K^+ \tag{8}$$

This reaction is even more complex in soil because of its natural organic and inorganic constituents that compete for the available oxidant. These non-target species not only consume the oxidant but may also result in complex reaction pathways possibly producing new contaminants [14].

Previous studies have concluded that TCE transformation by permanganate is pseudo-first-order with respect to both [TCE] and $\left[MnO_4^- \right]$ and second-order reaction overall (with a second order rate constant estimated

between 640 mM^{-1}·s^{-1} and 920 mM^{-1}·s^{-1}) [15] [16]. The expression for the second order rate law for the chemical oxidation of TCE by MnO_4^- is described in Equation (9) [10]-[12] [17].

$$\frac{d[TCE]}{dt} = -k_2 [TCE]\left[MnO_4^-\right] \tag{9}$$

According to Urynowicz, if the concentration of MnO_4^- does not change significantly with time (*i.e.* excess amount of MnO_4^-), Equation (9) can be simplified to pseudo-first-order to (10) by defining the pseudo first-order rate constant as the product of the second order reaction rate constant and the initial concentration of MnO_4^-.

$$\frac{d[TCE]}{dt} = -k_1 [TCE] \tag{10}$$

where
$k_1 = k_2 [MnO_4^-]$ = pseudo first-order reaction rate constant (s^{-1});
k_2 = second-order reaction rate constant (M^{-1}·s^{-1});
[TCE] = concentration of the TCE (M); and
$\left[MnO_4^-\right]$ = concentration of the MnO_4^-.

However, another way of obtaining the data for second-order kinetics analysis and rate constant (k) when A reacts with B as TCE and KMnO$_4$ respectively is given as follows:

$$-r = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B \tag{11}$$

$$-r_A = C_{AO}\frac{dX_A}{dt} = k\left(C_{AO} - C_{AO}X_A\right)\left(C_{BO} - C_{AO}X_A\right) \tag{12}$$

Let $M = C_{BO}/C_{AO}$ be the initial molar ratio of reactants, to obtain

$$-r_A = C_{AO}\frac{dX_A}{dt} = kC_{AO}^2 \left(1 - X_A\right)\left(M - X_A\right) \tag{13}$$

on separation and integration becomes

$$\int_0^{X_A} \frac{dX_A}{\left(1 - X_A\right)\left(M - X_A\right)} = C_{AO}k\int_0^t dt. \tag{14}$$

After breaking down into partial fractions, integration, and rearrangement, the final result in a number of different forms is

$$\ln\frac{M - X_A}{M\left(1 - X_A\right)} = C_{AO}\left(M - 1\right)kt = \left(C_{BO} - C_{AO}\right)kt \quad M \neq 1$$

Thus, the second order rate law is expressed as

$$\ln\frac{\left(M - X\right)}{M\left(1 - X\right)} = \left(C_{BO} - C_{AO}\right)kt \tag{15}$$

where C_{AO} is the initial TCE concentration (M); C_{BO} is the initial KMnO$_4$ concentration (M); $M = C_{BO}/C_{AO}$; X is the TCE percent conversion, $X = (C_{AO} - C_{At})/C_{AO}$ and C_{At} is TCE concentration at time t.

Some researchers have only presented the kinetics of the process which basically depends on the data analysis and interpretation. However, both the extent and kinetics of the oxidation process better express the efficiency of remediation techniques. Therefore, the specific objectives of this paper focused on: 1) to determine the extent and kinetics of TCE degradation by MnO_4^-; 2) to determine the impact of pH on the extent of TCE degradation by MnO_4^-; 3) to determine the effect of hexavalent chromium on TCE degradation by MnO_4^- and 4) to investigate controlled oxidation rate by PMMA encapsulated KMnO$_4$.

2. Materials and Methods

2.1. Chemical Preparation

In this study, Trichloroethylene, 100% (American Chemical Society, ACS grade), potassium permanganate (oxidant), sodium thiosulfate (used to quench reaction) and HPLC grade hexane (liquid-liquid extraction) were all purchased from Fisher Scientific. Bead particles of Poly (methymetacrylate) (PMMA) was ordered from Acros Organics; sodium borate and potassium dichromate purchased from Mallinckrodt, inc; Acetone (100%) was purchased from Acros Organics. Stock solutions of trichloroethylene were prepared as necessary by adding pure phase TCE to continuously stirred Milli-Q™ deionized water in a glass flask using a 6000 arrow magnetic stirrer. Similarly stock solutions of TCE in hexane were likewise prepared for calibration and other applications. Stock solution of potassium permanganate was prepared at 1000 ppm by adding 1000 mg of $KMnO_4$ particles to a liter of Milli-Q™ deionized water. While stock solution of sodium thiosulfate was prepared by adding sodium thiosulfate granules with Milli-Q™ deionized water. The stock solutions were stored in brown glass bottles and used fresh. Chelsea soil from Chelsea, Michigan was also used as received. Chelsea soil was spiked using a 40 ml amber vial with Teflon septa cover. 10 g of the soil was contaminated using a 30 ml of 10,000 mg/l of TCE solution in hexane and mixed for 48 hours to equilibrate. After 48 hours, the unabsorbed TCE/Hexane phase was separated from the soil and analyzed to determine the amount of TCE left in equilibrium.

2.2. Experimental Procedure

Kinetics and extent experiment were performed in serial batch reactors of 40 ml volatile organic analysis (VOA) vials with Teflon lined silicon septa. All experiments were performed at ambient temperature. Triplicate experiments were conducted for different molar ratios of TCE to $KMnO_4$ (1:2, 1:5, and 1:10) using up to 12 vials per experiment. Aliquots of the oxidant were added to TCE solution in each vial, which were then closed tightly and mixed on a rotary mixer. At predetermined time intervals, 1 ml the sodium thiosulfate, NaS_2O_3 solution were injected into the respective vials to quench the reaction and allow the analysis of TCE. Pure hexane of half the volume of sample solution was used to extract the TCE phase for analysis. Control vials containing only TCE solutions were analyzed at corresponding time intervals.

The extent of TCE degradation in soil system was also investigated at ambient temperature. 40 ml VOA vials were used as the serial batch reactors. Each experimental run was performed in triplicates and a control experiment was performed without MnO_4^-. MnO_4^- solutions were added to the 40 ml vials containing 2 g of TCE spiked soil. The concentration of spiked soil from artificial contamination was 16.27 ± 3.1 mg/g. The vials containing a mixture of MnO_4^- and TCE spiked soil were agitated continuously in a rotary mixer. At selected time intervals, sodium thiosulfate solution was injected into the appropriate vials and mixed to completely quench the reaction. Then, a predetermined volume of pure hexane was added to the sample, shaken for 2 minutes and then allowed to equilibrate for 10 minutes to extract the TCE residue. The hexane/TCE phase was therefore separated for TCE analysis on a gas chromatograph. The flow diagram for the experimental setup is shown in **Figure 1**.
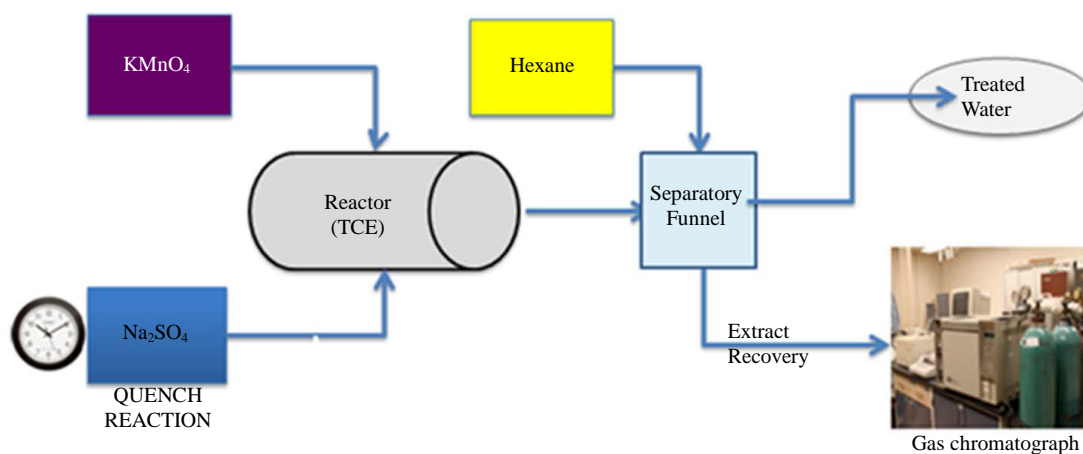

Figure 1. Process flow diagram for TCE degradation.

2.3. Encapsulation Procedure

KMnO$_4$ (oxidant) was encapsulated in PMMA matrix by adapting and modifying the molten suspension and cooling method at room temperature [18]. A predetermined amount (e.g. 2 g) of PMMA was measured into a 100 ml beaker and 3 ml acetone is added. The PMMA whose melting point is very high melts at room temperature under the influence of acetone. The molten PMMA is placed on a stirrer and mixed thoroughly using a glass magnetic arrow. Borax (Sodium Borate) was added to initiate cross-link of the molten PMMA. Under continuous mixing, particles of KMnO$_4$ were added as required to produce 1:2, 1:4 and 1:8 of KMnO$_4$ of PMMA ratio. After mixing for 10 mins to assume uniform particle dispersion, the molten mixture was allowed to solidify under room temperature by volatilizing acetone. Solidified particles/granules of encapsulated KMnO$_4$ were reduced and used as needed for the release and reaction experiments. The flow diagram (**Figure 2**) depicts the encapsulation process.

2.4. Analytical Procedure

TCE Concentrations were measured using gas chromatograph, HP 5890 Series II with a fused silica capillary column. The detector was electron capture detector (ECD) as recommended for chlorinated hydrocarbon. 2 µl aliquot of the pre-extracted TCE in hexane was injected in the injection port. The concentration for the integrated area associated with the peak was evaluated on a calibration curve. For the analysis, the detector temperature was 220; injection port was 200 while oven (column) temperature was 150˚C. The primary carrier gas was helium gas supported by nitrogen gas to maintain pressure head.

KMnO$_4$ concentrations were also measured to monitor the oxidant consumption rate. UV spectrophotometer (UV-166) set at 525 nm wavelength was used to measure KMnO$_4$ concentrations (recommended by Hood *et al*, 2000). Calibration curve was obtained for concentration (absorbance) points in the domain of 0 to 100 mg/l KMnO$_4$.

3. Results and Discussion

3.1. Extent of TCE Degradation by KMnO$_4$ in Aqueous and Soil Systems

The complete oxidation of TCE, equivalently optimal amount of permanganate is required not merely stochiometric ratios as presented by Equations (3.1)-(3.4). Minimizing the amount of MnO$_2$ produced from KMnO$_4$
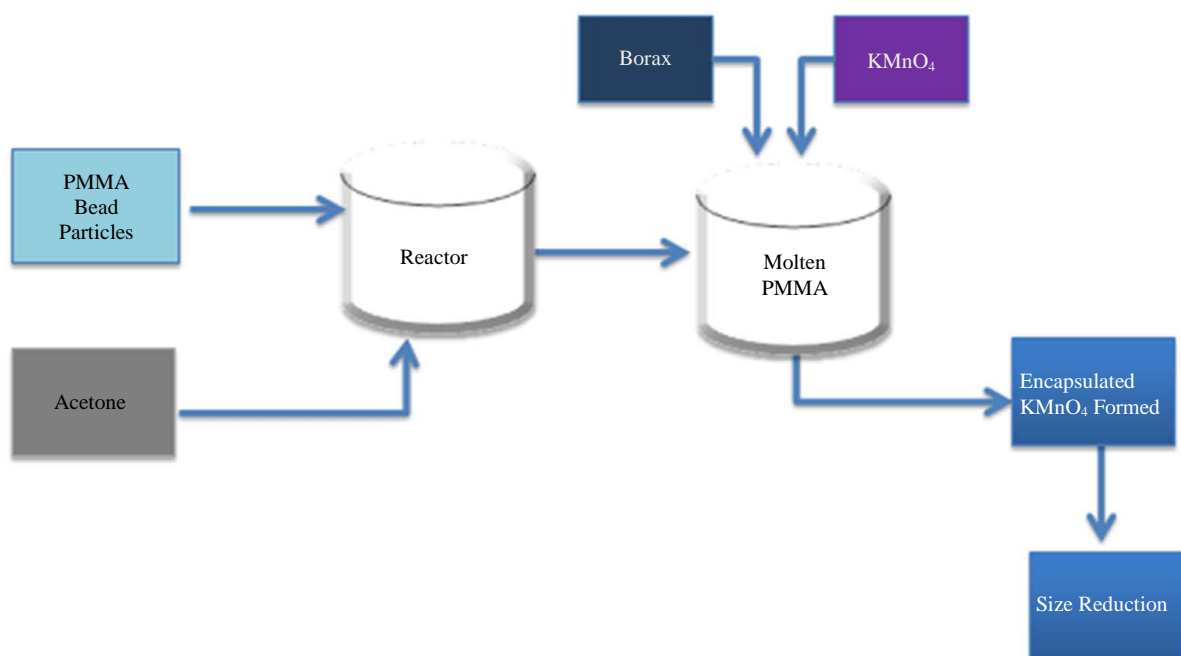

Figure 2. Encapsulation of KMnO$_4$ using PMMA.

is as important as the complete degradation of TCE. Therefore, the p-values help to determine the optimal $KMnO_4$ to TCE ratio required without excess oxidant. Using an initial TCE concentration (Co) of 100 and 600 ppm with p-values of 0, 2, 5, and 10, percent of TCE remaining was plotted against time. Result indicated that the higher p-value, the higher the extent of TCE degradation at equilibrium. When the initial TCE concentration was 100 ppm, for p values 2, 5, and 10, the effluent was left with 48%, 0.6% and 0.03% TCE respectively at a reaction time of 180 mins (**Figure 3**). This shows that the optimal p-value is 10 but a p-value of 5 could be the optimal value depending on the allowable or maximum contaminant level in the region of operation. While for Concentration of 600 ppm, for p-values 2, 5, and 10, the effluent was left with 37.5%, 0.021% and 0.02% TCE respectively at a reaction time of 180 mins (**Figure 4**). The optimal p-value is clearly 5 because p-value of 10 would be excessive use of oxidant ($KMnO_4$).

3.2. Influence of pH on the Extent of Reaction

The impact of pH on the system is not largely significant at stochiometric molar ratios. However, at high alkaline pH of 12.05 the percent conversion for TCE oxidation is low compared to acidic conditions. This could be
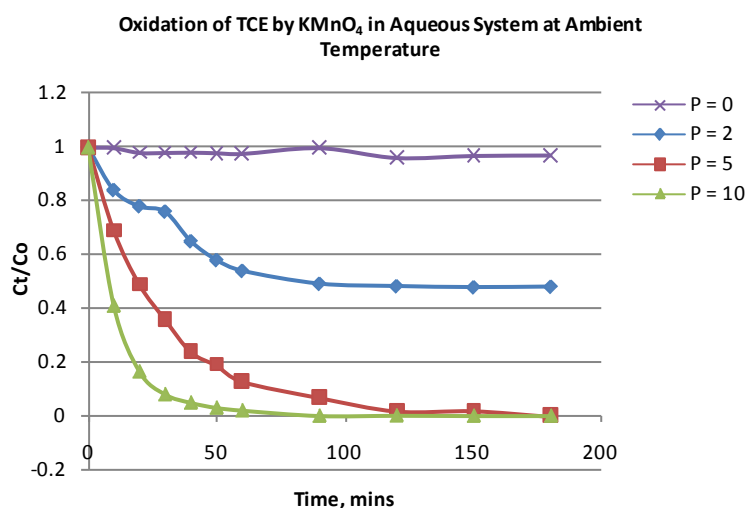
Figure 3. Extent (%) of TCE oxidation as a function of time with varying p-values (Initial concentration ~100 ppm).
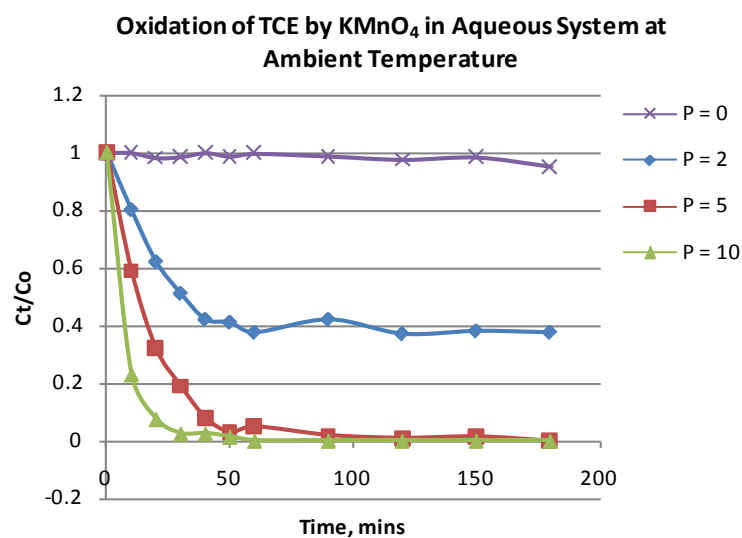
Figure 4. Extent (%) of TCE oxidation as a function of time with varying p-values (Initial concentration ~600 ppm).

attributed to the speciation or hydrolysis of MnO_4^- to MnO_2 under alkaline environments [11] [19]. The result in **Figure 5** shows that $KMnO_4$ is an effective oxidant across the pH range with slight variation likely due to speciation.

In soil systems, the efficiency of TCE degradation is very low. Only a small amount of TCE is degraded even after running the experiment for six hours. Other researchers proposed that this efficiency could even be lower for other types of soil such as clayey sand and silty-clay due to their pore sizes. In this study, a large amount of $KMnO_4$ was used to obtain the similar TCE Degradation in 60 hours. For a molar ratio of TCE to $KMnO_4$ of 1 to 5, 1 to 15 and 1 to 30, the percent TCE degraded were 62.8%, 96%, and 99.3% respectively after 2 days (**Figure 6**). This relatively lower TCE degradation rate in soil compared to aqueous system is attributed to the mass transfer limitation of the heterogeneous system.

3.3. TCE Oxidation in the Presence of Cr(VI)

TCE Oxidation by permanganate was not impacted by the presence of Cr(VI) possibly as both $KMnO_4$ and $K_2Cr_2O_7$ oxidizing agents although $KMnO_4$ is a much stronger oxidant (**Figure 7**). Since Cr(VI) is the only or dominant species present in $K_2Cr_2O_7$, therefore the primary oxidant is not consumed. Both $KMnO_4$ and $K_2Cr_2O_7$ are highly soluble in water and therefore equally occupy the oxidation interface. TCE oxidation by $KMnO_4$ yielded 65.75% and 62.5% in the presence and absence of Cr(VI) respectively. This experiment was not investigated under varying pH conditions which could influence Chromium speciation in aqueous phase. This is consistent with the hypothesis and results from Woojin Lee, 2004.
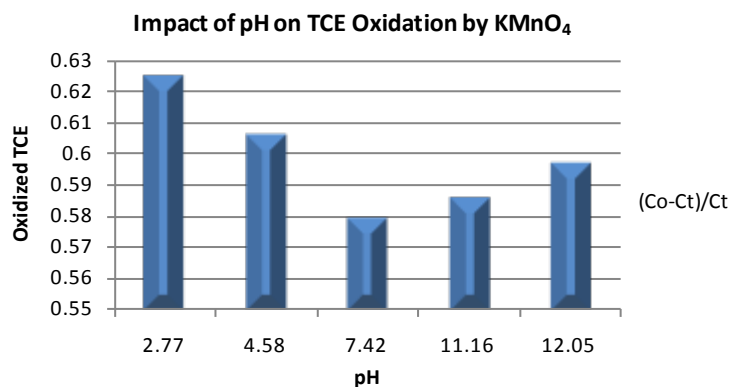

Figure 5. Influence of pH on the extent of TCE oxidation by $KMnO_4$.
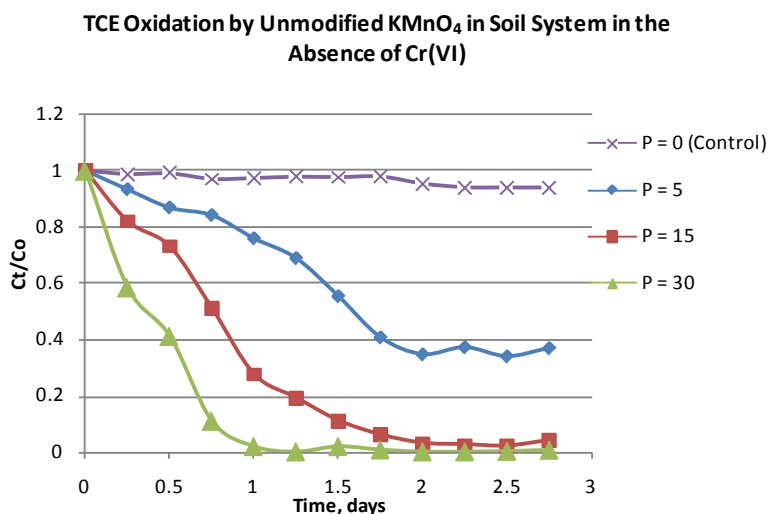

Figure 6. Extent (%) of degradation initial TCE concentration 16.27 mg/g (using 2 g of soil) (Initial TCE = 0.25 mmole).

3.4. Kinetics of TCE Degradation by KMnO₄

Figure 8 presents the plot of ln [(M − X)/(M(1 − X)] versus time for the p values of 2, 5, and 10 for an initial TCE concentration of 600 ppm. Following Equation (15), the second-order rate constants were calculated to be 441.67 mM^{-1}·s^{-1}, 491.83 mM^{-1}·s^{-1} and 496.4 mM^{-1}·s^{-1} for p value 2, 5 and 10 respectively. These k-values are lower than the range (600 mM^{-1}·s^{-1} to 920 mM^{-1}·s^{-1}) previously reported by other researcher [19] [20]. However, the near linear correlation indicated by the R^2 values of 0.97, 0.98 and 0.995 for the respective p-values implies a second-order overall reaction which had been reported [18] [20]. Therefore the differences in the rate constants can be attributed to equipment settings such as temperature of oven, injection and detector.

In soil system, the rate of the reaction is expectedly lower. **Figure 9** presents the plot of ln [(M − X)/(M(1 − X)] versus time for the p values of 5, 15 and 30. For a second-order reaction rate analysis, 0.457 kg·mole^{-1}·day^{-1} (5.287 × 10^{-6} kg·mole^{-1}·s^{-1}), 0.651 kg·mole^{-1}·day^{-1} (7.54 × 10^{-6} kg·mole^{-1}·s^{-1}) and 0.894 kg·mole^{-1}·day^{-1} (1.035 × 10^{-6} kg·mole^{-1}·s^{-1}) for the respective p-values.

3.5. Encapsulated KMnO₄ in Aqueous Medium

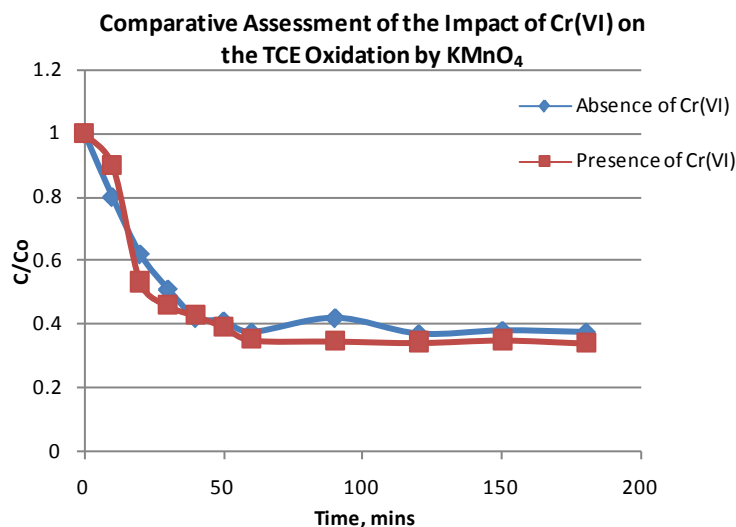The oxidant release experiment was performed in aqueous phase. KMnO₄ was released from PMMA encapsulation

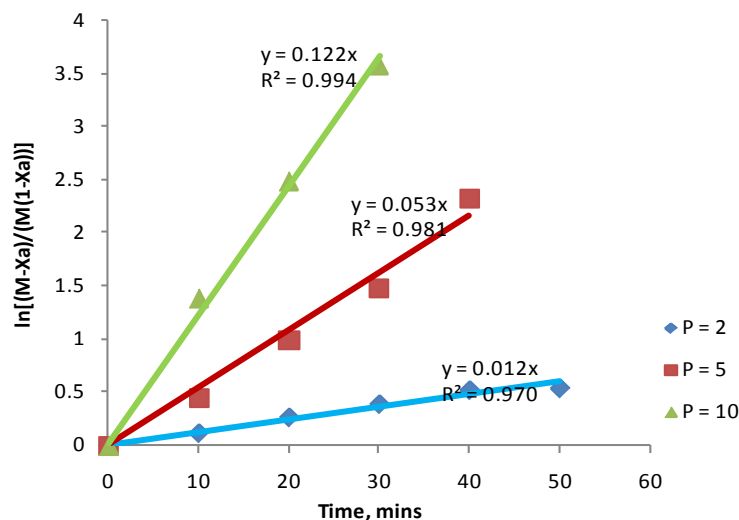**Figure 7.** TCE oxidation by KMnO₄ in the presence and absence of Cr(VI).

Figure 8. Kinetic analysis of TCE oxidation by KMnO₄ in aqueous phase.

in mass to mass ratios of 2:1, 4:1, and 8:1 of PMMA to $KMnO_4$ respectively. The release profile indicates that efficiency of the oxidant release is inversely proportional to the mass ratio of PMMA to $KMnO_4$. There was decrease in release with increased mass to mass ratio (see **Figure 10**). After a time period of 10 hours, 79%, 55.35% and 33.59% of $KMnO_4$ has been released from 2:1, 4:1, and 8:1 encapsulated matrix respectively. PMMA is not readily soluble in aqueous medium hence initial release near time $t = 0$ could be attributed to dissolution of $KMnO_4$ integrated on outer surface of encapsulated matrix. Results showed the lowest release rate is associated with 8:1 mass ratio likely due to the thickness of the PMMA layer in the encapsulated matrix.

3.6. TCE Oxidation by PMMA Modified $KMnO_4$ Simultaneously with Cr(VI) Reduction by $FeSO_4$

The Cr(VI) reduction by ferrous ion still shows its initial rapid reaction which stops on the accumulation of precipitate. There was 81% Cr(VI) reduced and 88% TCE oxidized by ferrous ion and permanganate respectively (**Figure 11**). This result compares to the result obtained for the independent redox reactions of TCE oxidation by $KMnO_4$ (see **Figure 3** and **Figure 4**). This could be attributed to the fact that PMMA dissolves in TCE but not
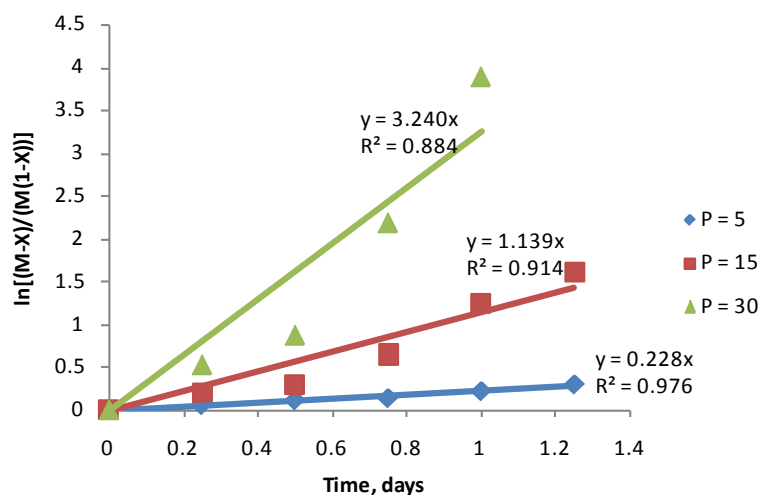

Figure 9. Kinetic analysis of TCE oxidation by $KMnO_4$ in chelsea soil.
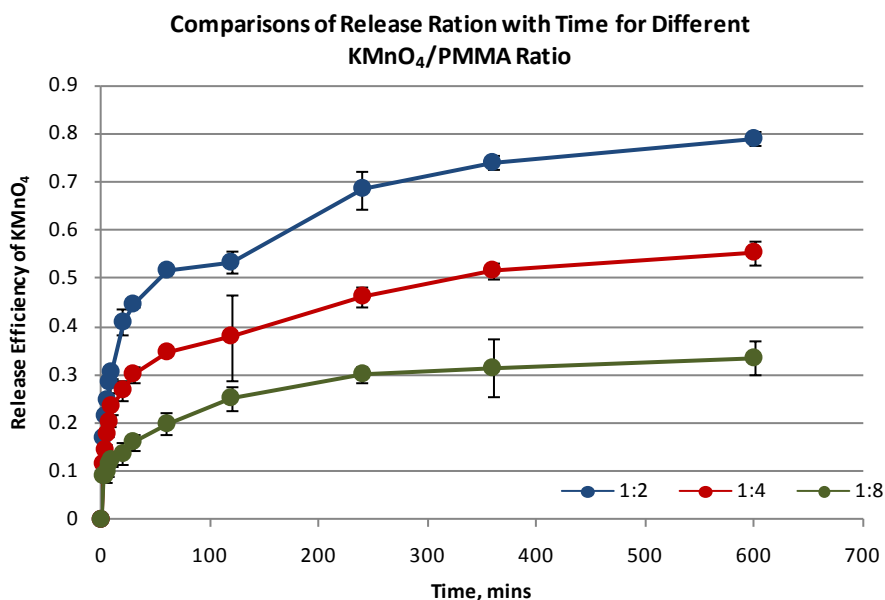

Figure 10. Release profile of $KMnO_4$ from PMMA encapsulation.

in water. Therefore on continuous interaction with TCE molecules the layers of PMMA could wear off from matrix releasing more $KMnO_4$ on contact. The availability of the oxidant depends on the dissolution and diffusion from layers of PMMA on contact with the TCE.

The efficiency of TCE degradation using PMMA modified $KMnO_4$ and unmodified $KMnO_4$ as function of time was plotted in **Figure 12**. The release rate for $KMnO_4$ from the encapsulated matrix into aqueous phase is expectedly slow which influences the rate of TCE oxidation.

4. Conclusions

The optimal concentration of oxidant required for TCE oxidation depends on the investigated p-values to prevent secondary contamination from using excess $KMnO_4$. The overall reaction implied second-order kinetics with near linear correlation indicated by R square values. The estimated efficiency or extent of oxidation increased with increased p-values. The extent of the reaction is not largely influenced by pH conditions. However, at alkaline media there is relatively lower efficiency attributed to manganese oxide particles deposited at the oxidation interface. The presence of Cr(VI) does not affect TCE oxidation by $KMnO_4$ in aqueous phase. Both
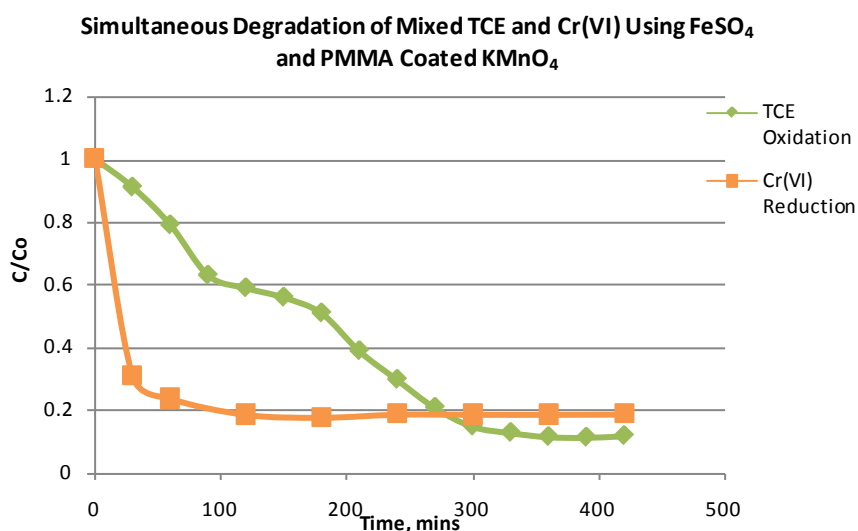

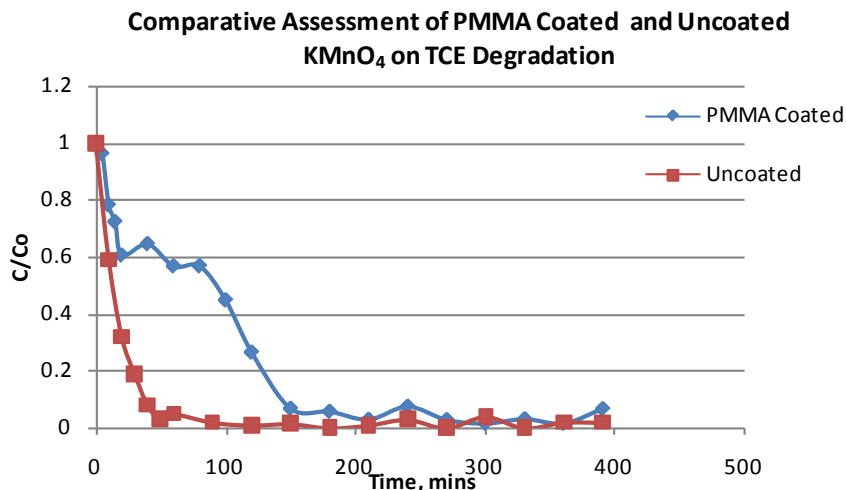**Figure 11.** Degradation of mixed TCE and Cr(VI) contaminants using modified $KMnO_4$.

Figure 12. Degradation of mixed TCE and Cr(VI) contaminants using unmodified $KMnO_4$.

KMnO$_4$ and K$_2$Cr$_2$O$_7$ are oxidizing agents and highly soluble in water. This could be responsible for the result obtained as both equally occupy the aqueous-TCE oxidation interface. In soil systems, the degradation is slower due to imposed mass transfer resistance and hence increased oxidant consumption.

PMMA was effective in controlling the instant dissolution of KMnO$_4$ in aqueous media. The release rate depends on the thickness of the PMMA layer on oxidant surface. Results showed that the encapsulation of KMnO$_4$ by PMMA using the modified molten suspension technique controlled the rate of dissolution of KMnO$_4$ and improved the selective interaction between TCE and the KMnO$_4$. The amount of TCE oxidized increased in mixed contaminant degradation but at much longer time to achieve similar result unmodified KMnO$_4$. Thus, the PMMA encapsulated KMnO$_4$ can be used to target TCE in a mixed contamination. This study provides insight into the use of PMMA for different applications 1) for oxidant persistence in the long-term contamination problem of TCE; 2) for improved preferential interaction of oxidant with target contaminant based on environmental responsive condition.

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