Degradation of TCE using Persulfate (PS) and Peroxymonosulfate (PMS): Effect of Inorganic Ions in Groundwater

Ki-Man Park, Hong-Kyun Lee, Si-Hyun Do, Sung-Ho Kong*

Abstract — **The objective of this study was to investigate the effects of inorganic ions on persulfate (PS) and peroxymonosulfate (PMS) oxidation to degrade trichloroethylene (TCE) in groundwater. First, the groundwater samples, which was taken from Wonju, Korea, were analyzed, and the highest concentration of target ions (Mg^{2+}, Ca^{2+}, Fe^{2+}, Mn^{2+}, Cl^-, HCO_3^-) in those samples were used for the batch experiment. Based on batch test, all of target ions did not neither increase nor decrease the reactivity of both PS and PMS. Because of the fluctuation of groundwater compositions, it could be worthwhile to evaluate which ions increase or decrease the reactivity of oxidants. Therefore, a batch system with an excess of target ion was tested. The results showed that ferrous ion increased the reactivity of both PS and PMS. However, chloride ion increased the reactivity of PMS, but it inhibited the reactivity of PS. Moreover, residual concentration of PMS and PS were remained approximately 97~98%, and the pH of system was dramatically reduced when PMS was used. The last of target ions (Mg^{2+}, Ca^{2+}, Mn^{2+}, HCO_3^-) will be also tested with the condition of an excess.**

Keywords: magnetite nano particle (MNP), heterogeneous Fenton system, hydroxyl radical

I. INTRODUCTION

Trichloroethylene (TCE) has been widely used as dry cleaning solvent and industrial washing solution. However, it is a groundwater pollutant currently which has been widespread throughout aquifer due to diffusion of flow. Chemical treatments such as Fenton's reagent and potassium permanganate have been used for treatment of chlorinated compounds contaminated groundwater. Recently, remedial alternatives were needed so that both persulfate (PS) and peroxymonosulfate (PMS) which were based on advanced oxidation process (AOP) can be activated to generate powerful oxidant, sulfate radical ($SO_4^{\cdot -}$) [1, 2]. Both PS and PMS were relatively stable with the changes of the pH and these could be activated by UV, heat, and metal ions. PS oxidation reaction for degradation of organic compounds was accelerated by adding Ag^+, Fe^{2+}, and iron-chelate agent [3]. In case of PMS, it has been estimated that addition of Co^{2+} could be activated the PMS to degrade organic compounds [4]. In this research, degradation of TCE using PS and PMS oxidation under existing various inorganic ions was investigated. Effects of inorganic anions and inorganic cations were mainly tested whether what kinds of ions were influenced to degrade TCE with positive effect or not.

II. MATERIALS AND METHODS

2.1. Materials

Trichloroethylene (TCE, +99%), sodium persulfate (≥98%), Oxone®(95%) were purchased from Sigma-Aldrich Inc. Extraction solvent, n-hexane (95%) was purchased from J.T. Baker. $CaSO_4.\ 2H_2O$, $MgSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$, and $MnSO_4 \cdot H_2O$ were used as a inorganic cations. Both NaCl and $NaHCO_3$ were used as a inorganic anions and all agents were reagent grade. All solutions were prepared with deionized (DI) water using 18 MΩ·cm AquaMax systems (Young-Lin Instrument Co., Korea). Experiments were conducted in 0.8 L custom-made reactor. The reactor was made of stainless steel and which diameter is 6.52 cm and height was 24 cm.

2.2. Compositions of groundwater

The real groundwater samples were taken from Wonju, Korea and its characteristics are presented Table 1. Cations such as Ca^{2+}, Mg^{2+}, Fe^{2+}, and Mn^{2+} and anions such as Cl^- and HCO_3^- were mainly presented in those samples and target ions were used for the batch experiments. Moreover, target ion was adopted as same concentration of groudwater sample, and then further experiment was conducted by excess concentration of target ions to determine effects of ions precisely.

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2.3 Experimental procedures

TCE (0.076 mM, 10 ppm) and inorganic ions (Mg^{2+}, Ca^{2+}, Fe^{2+}, Mn^{2+}, Cl^-, and HCO_3^-) were mixed to make reaction mixture, and then total solution was poured into 0.8 L reactor. Small portion of solution was removed from reactor for injecting oxidant solution, and then reaction was initiated after adding oxidants (0.1M PS and 0.1M PMS). The reaction was conducted atmosphere pressure and temperature was maintained 25℃ by circulating system with vigorous stirring. Dissolved TCE in aqueous phase was extracted by n-hexane (liquid/liquid extraction). The residual TCE was analyzed using Agilent 6890N gas chromatograph (GC) equipped with an electron capture detector (ECD) and HP-5 column (30 m x 0.53 mm). Nitrogen was used as carrier gas. Residual PS was measured by spectrophotometric method (50 to 1800 mg/L). The absorbance was read with a spectrophotometer (Milton Roy Spectronic 10+) at a wavelength of 450 nm. Also, PMS was detected by PS analysis method.

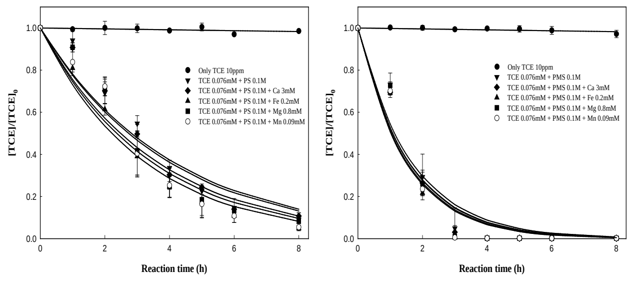
Table 1. Characteristic of inorganic ions containing groundwater samples

Species	Concentration ppm (mM)
Ca^{2+}	16-124 (0.39-3)
Mg^{2+}	2-20 (0.08-0.8)
Fe^{2+}	0-11 (0-0.2)
Mn^{2+}	0-5 (0-0.09)
Cl^-	4-295 (0.12-8.5)
HCO_3^-	14-149 (0.23-2.5)

III. RESULTS AND DISCUSSIONS

3.1. Influence of inorganic cations

Fig.1 and Table 2 show the results of influence of cations on the TCE degradation using PS and PMS. Degradation rate of TCE using PMS was more faster than using PS.



(a) (b)

Fig. 1. Influence of the inorganic cations on the degradation of TCE by oxidants; (a) PS, (b) PMS.

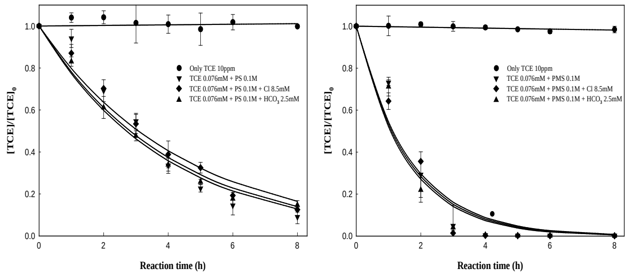
The degradation rates of TCE was $0.25h^{-1}$ using only PS (0.1M) (Table 2). Moreover, various cations such as Fe^{2+}, Mg^{2+}, and Mn^{2+} were added to degrade of TCE, the degradation rates were $0.31h^{-1}$, $0.27h^{-1}$, and $0.29h^{-1}$, respectively (Table 2). As a results of applying to PMS, the degradation rate of TCE was $0.60h^{-1}$ using only PMS. When addition of various cations was performed, the degradation rates of TCE were similar on all case of cations (Ca^{2+}: $0.63h^{-1}$, Fe^{2+}: $0.67h^{-1}$, Mg^{2+}: $0.63h^{-1}$, and Mn^{2+}: $0.66h^{-1}$) (Table 2). It seems that concentration of inorganic cation which was contained real groundwater does not affected to both PS and PMS oxidation for degrading TCE. Residual concentration of oxidants (PS and PMS) were remained approximately 97-98% after 8 h of reaction time. Moreover, the pH of system was decreased in case of PMS (pH 2). It seems to be quite all right to consider the protons released in the reaction of SO_4^{-}· with water [5].

Table 2. The results of TCE degradation by oxidants with inorganic cations

Oxidants [0.1M]	Conditions	Removal efficiency (%)	*k* (h^{-1})	Oxidants remaining (%)	Initial pH	Final pH
PS	-	91	0.25	97	7.1	6.4
	Ca^{2+} [3mM]	91	0.25	98	7.0	6.3
	Fe^{2+} [0.2mM]	95	0.31	97	6.7	5.8
	Mg^{2+}[0.8mM]	92	0.27	97	6.9	6.3
	Mn^{2+}[0.09mM]	95	0.29	98	7.0	6.1
PMS	-	99	0.60	98	7.1	2.3
	Ca^{2+} [3mM]	99	0.63	97	7.0	2.3
	Fe^{2+} [0.2mM]	99	0.67	98	6.7	2.4
	Mg^{2+}[0.8mM]	99	0.63	97	6.9	2.3
	Mn^{2+}[0.09mM]	99	0.66	97	7.0	2.3

3.2. Influence of inorganic anions

As shown in Fig. 2 and Table 3, the results of effects of inorganic anions (HCO_3^- and Cl^-) on the oxidation of TCE using both PS and PMS were demonstrated.



(a) (b)

Fig. 2. Influence of the inorganic anions on the degradation of TCE by oxidants; (a) PS, (b) PMS.

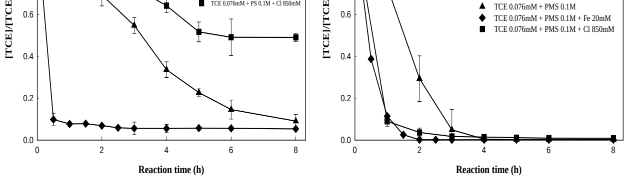
Degradation rates of TCE using only PS and PMS were $0.25h^{-1}$ and $0.60h^{-1}$. PS oxidation was not influenced by presence of HCO_3^- ($0.25h^{-1}$). Also, chloride ion (Cl^-) did not inhibit the degradation rate of TCE ($0.22h^{-1}$). As a result of PMS experiments, both Cl^- and HCO_3^- could not be influenced degradation rate of TCE (Cl^-: $0.62h^{-1}$, HCO_3^-: $0.65h^{-1}$). Thus, there is no difference both PS and PMS oxidation according to inorganic anions. It can be seen that inorganic anions did not influence to degrade TCE in aqueous phase at the same concentration of groundwater sample. TCE degradation rate using PMS oxidation was faster than using PS oxidation. It could be explained that PMS has an unsymmetric structure, it can be transformed by SO_3 [5]. Therefore, PMS is changed to strong oxidizer [5].

Table 3. The results of TCE degradation by oxidants with inorganic anions

Oxidants [0.1M]	Conditions	Removal efficiency (%)	k (h^{-1})	Oxidants remaining (%)	Initial pH	Final pH
PS	-	91	0.25	97	7.1	6.4
	Cl^-[8.5mM]	87	0.22	97	7.1	5.9
	HCO_3^-[2.5mM]	85	0.25	98	8.0	7.0
PMS	-	99	0.60	98	7.1	2.3
	Cl^-[8.5mM]	99	0.62	98	7.0	2.2
	HCO_3^-[2.5mM]	99	0.65	98	8.0	1.8

3.3. Evaluation of positive and negative effects using excess inorganic ions for degradation of TCE

When concentration of inorganic ions was existed as a same concentration of groundwater sample, it was not influenced to TCE degradation. Therefore, inorganic ions were spiked to observe effects of inorganic ions clearly using 100 times of groundwater sample concentration. Fig. 3 shows that excess of ferrous ion (20 mM) and chloride ion (850 mM) were injected on TCE oxidation using PS and PMS. Removal efficiency of TCE was 90% using PS, initial reaction was rapidly achieved within 30 min due to excess of ferrous ion. When excess of chloride ion was existed, degradation rate and removal of TCE were decreased (87% to 50%). On the other hand, results of PMS oxidation reveal that positive effects was presented, when excess of both ferrous ion and chloride ion was injected (99% degradation within 2h using Fe^{2+}). The oxidants for degradation of TCE consumed only 2%. In further study, inorganic cations (Mg^{2+}, Ca^{2+}, and Mn^{2+}) and anion (HCO_3^-) will be tested to give an excess concentration of inorganic ions.



(a) (b)

Fig. 3. Evaluation of positive and negative effects using excess inorganic ions for degradation of TCE; (a) PS, (b) PMS.

IV. CONCLUSION

Various inorganic ions were investigated to find positive or negative effects on PS and PMS oxidation for degradation of TCE. Inorganic ions were not influenced to degrade TCE at the same concentration of groundwater containing inorganic ions. On the other hand, the experimental results of degradation of TCE by injection of excess inorganic ions indicated that ferrous ion accelerated both PS and PMS oxidation rapidly degradation within 30 min, however the results of chloride ion presented negative effect to PS oxidation. Consequently, both PS and PMS oxidation may not be influenced in real groundwater containing various inorganic ions. However, when these ions were existed with high concentration, PS oxidation was influenced by ferrous ion (positive effect) and PMS oxidation was influenced by ferrous ion (positive effect) and chloride ion (positive effect). Therefore, prior to application of PS and PMS, a site should be investigated for inorganic ions containing groundwater, and then selection of oxidant should be performed.

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