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Trichloroethylene removal from water by ferrate treatment

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Abstract
In this study trichloroethylene (TCE) removal from model solutions and groundwater by ferrate treatment was investigated applying different initial TCE concentrations, ferrate dosages and pH values. TCE concentrations were measured both in the vapor and liquid phases of water samples with head space gas chromatograph mass spectrometer (HS/GC-MS) and solid phase micro-extraction gas chromatograph mass spectrometer (SPME/GC-MS) systems, respectively. Analytical data obtained by these methods were in good agreement and
the deviations changed in the range of 1 and 7%. The optimum pH value for the ferrate treatment was pH=7. Applying ferrate in concentration of 50 mg/L for treatment of model solutions with TCE concentration of 0.1 and 1.0 mg/L (FeO$_4^{2-}$/TCE molar ratios 500 and 50), the removal efficiency values were 97 and 74%, respectively. However, in case of groundwater having the same TCE concentrations but additionally 28 mg/L organic carbon content, the removal efficiency decreased to 42 and 36%. It means the necessary ferrate dosage considerable depends on the chemical composition of contaminated groundwater to be treated.
1. Introduction

Trichloroethylene (TCE) is a potentially carcinogenic and volatile organic chlorinated hydrocarbon (VOC), which have been used for several industrial purposes such as paint stripper, metal degreaser, chemical intermediate, and industrial cleaning agent. Due to its long-term and widespread applications, TCE became a typical contaminant both in surface and groundwater (Aulenta et al. 2005; Löffler et al. 2006).

For quantitative determination of TCE in different water matrices several sample-preparation and analytical methods are available. USEPA 551.1 Standard Method prescribes the application of liquid-liquid extraction (LLE) with methyl-tert-butyl ether or pentane. For analysis gas chromatograph (GC) coupled with electron capture detector (ECD) or mass spectrometer (MS) are recommended (Munch et al. 1995). LLE with diethyl-ether and GC-MS were used to quantify TCE concentration in drinking water (Brown et al. 2003). Due to its high volatility, TCE can simply be determined with headspace (HS) GC technique or following an enrichment by solid phase micro extraction (SPME) also with GC introducing the loaded SPME fiber directly into the GC-injector port. These analytical techniques can be characterized with detection limits of 0.01-0.02 µg/L. (Peccorino et al. 2008; Gonzalo et al. 2008)

Over the past few decades for removal of TCE from water matrices several technologies based on biodegradation and chemical oxidation (ozone, persulfate, ferrate) have been developed. Mészáros et al. applied Sulfurospirillum halorespirans and Dehalococcoides sp. communities for biodegradation of TCE in groundwater. 95% removal efficiency was achived and as by-products vinyl-chloride and ethane were detected (Mészáros et al. 2013). Ozonization combined with γ-radiation was also successfully applied to remove TCE from drinking water with efficiency of 98% (Gehringer et al. 1988). Liang et al. published three papers in topic of TCE removal applying activated persulfates. Depending on the activation way the TCE degradation rate changed from 65 to nearly 100 % in case of model solutions (Liang et al. 2003; Liang et al 2004a; Liang et al. 2004b). Although an efficient degradation of target molecules can be achieved by oxidation technologies mentioned above, the possible by-products remain in the treated solutions. Therefore it is recommended to apply an adsorption stage (e.g. filtration through activated carbon column) after oxidation.

Ferrate technology offers a simple way for water treatment by combination of oxidation and coagulation processes (Jiang et al. 2002; Lee et al. 2004; Jiang et al. 2007). The applicability
of ferrate for removal of heavy metals (Lim et al. 2010), cyanide (Lee et al. 2009), hydrogen sulfide (Sharma et al. 1997), ammonia (Sharma et al. 1998), arsenic (Lee et al. 2003) or organic contaminants e.g. biphenol-A (Li et al. 2008), carbohydrates (Sharma et al. 2012), phenol and chlorophenols (Graham et al. 2004), pharmaceutical residues (Sharma et al. 2006), personal care products (Yang et al. 2012) was demonstrated in the literature. It should be emphasized that the removal efficiencies were highly dependent on the testing conditions, the chemical properties of target molecules and the water matrix.

Only a few studies have been dealing with the removal of TCE by ferrate from aquatic solutions. DeLucca et al. investigated the TCE removal from model solutions containing 0.5 meq/L NaHCO₃, about 1.0 mg/L total organic carbon (TOC) and 0.1: 0.32 and 1.0 mg/L TCE by means of potassium ferrate added in concentration of 10, 20 or 30 mg/L at pH 8.3. At FeO₄²⁻/TCE molar ratio of 182:1 the ferrate oxidation-coagulation processes followed by gas (N₂) flocculation resulted in practically a full removal of TCE (DeLucca et al. 1983). However, it should be noted, that during the gas flocculation a considerable amount of TCE could be volatilized. The study of Graham et al. was focused on the influence of pH on the degradation of TCE as a non-dissociating compound, by potassium ferrate in the K$_2$FeO$_4$/TCE molar ratio range of 1:1 to 9:1. It was established that the extent of degradation achieved a maximum at pH 8 and about 85% of TCE was removed at molar ratio of 9:1. The lower degradation of TCE in acid or neutral conditions, where the oxidation potential of the ferrate is high, was explained by the high rate of ferrate decomposition. (Graham et al. 2004)

Nam et al. studied TCE degradation rate in model solutions with electrochemically generated ferrate at various pH values. According their results in case of 1.0 mg/L initial TCE concentration the removal efficiency was 64% applying potassium ferrate in concentration of 17 mg/L FeO$_4^{2-}$/TCE molar ratio 17:1 at pH=7 and treatment time of 30 minutes. As intermediate products ethyl chloride, dichloroethylene, chloroform, 1,1-dichloropropene, trichloroacetic acid, trichloroethane, and as end product Cl⁻ were identified (Nam et al. 2012). In this work TCE removal from model solutions and spiked groundwater obtained from a chlorinated hydrocarbons contaminated area was studied using potassium ferrate solution generated by electrochemical reactions. Our goal was to develop a technology based on oxidation-coagulation processes for treatment of polluted groundwater and to select an appropriate analytical method to follow the TCE degradation comparing the HS-GC-MS and SPME-GC-MS methods. Since the contaminated groundwater has a relatively high total organic carbon content which also consumes the ferrate reagent, in our experiments a higher ferrate /TCE ratios were selected than in the papers mentioned above.
2. Materials and Methods

2.1. Chemicals

All chemicals used during the experiment were of analytical grade. Trichloroethylene was purchased from Sigma Aldrich Ltd., Hungary, and for its dissolution ultrapure water was used produced by Milli Q Plus equipment. Potassium ferrate solution was produced by electrochemical process in our laboratory. For pH adjustment sulfuric acid solution and to regulate the buffer capacities of model solutions sodium-hydrogen-carbonate were applied.

2.2. Solution preparation and handling

Model solutions containing TCE in concentration of 0.1 and 1.0 mg/L were prepared by using ultrapure water and trichloroethylene. In order to achieve a similar buffer capacity of these solutions to the groundwater, sodium hydrogen carbonate was added in concentration of 600 mg/L to these model solutions. In this way similar inorganic carbon content was set for both systems. Groundwater was filtered through a glass membrane (Millipore, 0.45 µm), and analyzed by methods listed in 2.4 subchapter. Since TCE was not detectable in the groundwater containing several other chlorinated hydrocarbons, TCE was added to this groundwater resulting in concentration of 0.1 and 1.0 mg/L. After this process 10 cm$^3$ of each water sample was transferred into a septum sealed vial with volume of 20 cm$^3$.

2.3. Analytical instruments and operating conditions

The analysis was carried out by a Bruker SCION 436 GC-MS system, equipped with a SHS-40 headspace autosampler. Separation of the compounds was obtained on a BR-5 column (30 m × 0.25 mm, df=1 µm) using helium (purity: 6.0, which means He of: 99.9999%) as carrier gas (flow rate 2 ml/min). The temperature of manifold, filament and transfer line was 40°C, 200°C, 220°C, respectively. Analytical measurements were performed in scanning mode (m/z: 50–500).

TCE concentration in the vapor phase was determined applying headspace autosampler. To achieve a steady state distribution of analyte between the vapor and liquid phase the sample was thermostated at 40°C for 1 minute and 1 cm$^3$ vapor sample was injected to the GC-MS system. Column temperature program started at 60°C maintained for 6 minutes, then ramped at 10°C/min up to 100°C (total elution time was 10 minutes). Injector temperature and split ratio were 250°C and 1/10, respectively.
TCE concentration in liquid phase was measured applying SPME fibers (Supelco, PDMS, 100 µm). Before the first application, SPME fiber was conditioned in the GC-MS injector port at 250°C for 30 min. After that the SPME fiber was introduced into the septum sealed vial containing 10 cm³ water sample and immersed into the solution at room temperature for 5 minutes, then directly injected to the GC-MS port. Between each measurement the SPME fiber was conditioned at 250°C for 5 minutes. GC-MS temperature program started at 40°C maintained for 0.75 minutes, then ramped at 20°C/min up to 160°C (total elution time was 6.75 min). Injector temperature was 230°C and splitless mode was used.

2.4. Chemical analysis of groundwater
The groundwater was obtained from a hydrocarbon contaminated area and before the treatment process its physico-chemical parameters were determined according to standard methods. Total inorganic carbon (TIC), total organic carbon (TOC), as well as total nitrogen (TN) concentrations were measured by applying a Multi N/C 2100S TC-TN analyzer (Analytik Jena, Germany) equipped with a non-dispersive infrared detector (for C) and a chemiluminescent detector (for N) according to the valid international standards (EN ISO 5667-3:1995 and MSZ EN 12260:2004). Specific electric conductivity and pH were characterized according to standard methods. (APHA, AWA, WEF 2005) Organic hydrocarbon content of the groundwater was identified according to HS/GC-MS method as mentioned in subchapter 2.3.

2.5. Ferrate treatment
10 cm³ model solutions or spiked groundwater having 0.1 or 1.0 mg/L initial TCE concentrations were introduced into septum sealed vials. After that calculated amount of ferrate solution was added to these water samples by using an injection syringe resulting in 10, 20, 30 and 50 mg/L ferrate concentrations. Similar manner the pH was adjusted to 3, 5, 7, 9 or 11 by addition of sulfuric acid and the solutions were agitated with Teflon coated magnetic stirrer bar for 30 minutes. After 1 minute stabilization time the TCE concentration was measured in the vapor phase by HS-GC-MS. The TCE determination in the liquid phase by SPME-GC-MS method needed 15 minutes for sedimentation of the reduced Fe(III) compounds.
3. Results and discussion

3.1. Chemical analysis of groundwater

Before ferrate treatment the physical-chemical parameters of groundwater: total inorganic carbon, total organic carbon, total nitrogen, pH, specific electric conductivity were determined according to standard methods. Analytical data are listed in Table 1. As main organic hydrocarbon contaminants: 1.1 dichloroethylene, 1.2-cis dichloroethylene and 1.2-trans dichloroethyelene were identified according to above mentioned HS/GC-MS method in subchapter 2.3.

3.2. Optimum pH value establishment of ferrate treatment

In order to establish the optimum pH for the ferrate treatment, model solutions having 0.1 mg/L were reacted with ferrate at different concentration and pH (see subchapter 2.5). TCE concentration in the treated solutions was measured by HS/GC-MS technique. The removal efficiencies obtained at various pH values and ferrate concentration are presented in Fig. 1. It can be established that the highest removal efficiency values were achieved at pH=7 and the concentration of ferrate had only moderate influence on the TCE removal in the pH range 5-9. However, at pH=3 and 12, were the ferrate compounds is instable or even stabilized, respectively, the increasing ferrate concentration resulted in higher removal efficiency of TCE. Considering these results all further ferrate treatments were carried out at pH=7.

3.3. TCE removal from model solutions

Model solutions having 0.1 and 1.0 mg/L TCE initial concentrations were prepared as mentioned in subchapter 2.2, and treated by ferrate at concentration of 10, 20, 30, 50 mg/L applying intensive magnetic stirring for 30 minutes at pH=7. After the oxidation process TCE residues was measured both in the vapor and the liquid phase. The removal efficiency values are illustrated in Fig 2. These analytical data demonstrate the excellent analytical features of the HS and SPME sampling procedures for determination of TCE. At 20 mg/L ferrate and 0.1 mg/L TCE concentrations 97 and 96% removal efficiencies were measured applying these analytical methods. Increasing the TCE concentration to 1.0 mg/L the removal efficiency decreased to 74 and 73% following the same ferrate treatment. It means it is not recommended to use higher ferrate concentration than 20 mg/L.
3.4. TCE removal from groundwater

After chemical analysis and filtration of groundwater as mentioned in subchapter 2.2, the water samples were spiked with TCE similarly to the model solutions. Ferrate treatment process was carried out under the same conditions as in the case of model solutions. The residues of TCE were measured both in the vapor and liquid phases. The analytical results are presented in Fig 3.

It can be seen, that in presence of organic matrix compounds the TCE removal increased contrary of model solution treatment, adding more ferrate dosages, higher TCE removal can be achieved. Results demonstrate, that samples having 0.1 mg/L initial TCE concentration, in the vapor- and liquid phases removal efficiency were 42%, and 41% by adding 50 mg/L ferrate dosage. Applying one magnitude higher TCE concentration and using same circumstances the degradation rate were 35% and 38%, respectively. It can be seen, that in case of samples having 0.1 mg/L TCE concentration, higher removal can be achieved but it should be emphasized, that this rate is lower than in case of model solution. It can be also concluded, that similarly to treatment of model solutions the vapor and liquid phase measurements also correlated with each other.

3.5. Comparing TCE removal efficiencies obtained for model solutions and spiked groundwater

In Fig 4. TCE removal efficiencies are presented applying 50 mg/L ferrate concentration for treatment of model solutions and spiked groundwater having two different initial TCE concentrations.

It can be stated, that the removal efficiency decreased with increasing concentration of analyte. For example the reduction of ferrate/TCE concentration ratio from 500 to 50 resulted in removal efficiency from 97 to 74% in case of model solutions. However, this picture became more sophisticated in presence of dissolved organic and inorganic compounds which also consume the oxidation agent. Therefore the estimation of the necessary amount of ferrate for a successful purification procedure of contaminated groundwater needs a preliminary analytical investigation. First of all the TOC content plays a decisive role.
4. Conclusion

Experimental data showed that both the HS/GC-MS and the SPME/GC-MS are appropriate analytical techniques to follow the concentration changes of TCE both in the contaminated and the ferrate treated groundwater samples. Comparing TCE removal from model solutions and groundwater samples, it can be concluded, that the organic groundwater matrix hampers the degradation of target molecules by oxidation. This phenomenon can be attributed to contaminants with similar or higher electron donor capacity than TCE. In order to develop an environmental friendly ferrate treatment technology for removal of TCE from contaminated groundwater in the next step the chlorine containing by-products will be identified and the chlorine balance will be calculated.
References


Table 1. Physical-chemical parameters of groundwater

<table>
<thead>
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<th>Parameter</th>
<th>Value</th>
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<td>Total inorganic carbon (mg/L)</td>
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<td>Total organic carbon (mg/L)</td>
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<td>Total nitrogen (mg/L)</td>
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<td>pH</td>
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<tr>
<td>Specific electric conductivity (µS/cm, 20°C)</td>
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Fig 1.
Fig. 2.
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Fig. 1. TCE removal efficiency from model solution containing TCE in concentration of 0.1 mg/L at various pH and ferrate dosages; Analytical data were determined by HS-GC-MS.

Fig. 2. TCE removal efficiency from model solutions having 0.1 and 1.0 mg/L initial TCE concentrations at pH=7 and various ferrate dosages; Analytical data were measured by both HS-GC-MS and SPME-GC-MS methods.

Fig. 3. TCE removal efficiency from spiked groundwater containing 0.1 and 1.0 mg/L TCE at pH=7 and various ferrate dosages; Analytical data were measured by both HS-GC-MS and SPME-GC-MS methods.

Fig. 4. TCE removal efficiency from model solutions and spiked groundwater at pH=7 and ferrate concentration of 50 mg/L measured by HS-GC-MS.