Trichloroethylene removal from water by ferrate treatment

Péter Dobosy [a,b], Éva Cseperke Vizsolyi [b,c], Imre Varga [b], József Varga [c], Győző G. Láng [d], Gyula Záray [b,*]

[a] MTA Centre for Ecological Research, Danube Research Institute, Karolina út 29-31, H-1113 Budapest, Hungary
[b] Cooperative Research Centre of Environmental Sciences, Eötvös Loránd University, Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary
[c] IMSYS Ltd., Mozaik u. 14/a, H-1033 Budapest, Hungary
[d] Institute of Chemistry, Laboratory of Electrochemistry and Electroanalytical Chemistry, Eötvös Loránd University, Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary

ARTICLE INFO

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 only 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 with an additional 28 mg/L organic carbon content, the removal efficiency decreased to 42% and 36%. This means that the necessary ferrate dosage considerably depends on the chemical composition of the contaminated groundwater to be treated.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Trichloroethylene (TCE) is a potentially carcinogenic and volatile organic chlorinated hydrocarbon (VOC), which has been used for several industrial purposes such as paint stripper, metal degreaser, chemical intermediate and industrial cleaning agent. Due to its long-term and wide-spread applications, TCE has become a typical contaminant both in surface and in groundwater [1–2].

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) is recommended [3]. LLE with diethyl-ether and GC–MS were used to quantify TCE concentration in drinking water [4]. Due to its high volatility, TCE can simply be determined with headspace (HS) GC technique [5]. The enrichment of TCE by solid phase micro extraction (SPME) and the introduction of loaded SPME fiber directly into GC-injector port offer also a promising way for TCE analysis [6]. These analytical techniques can be characterized with detection limits of 0.01–0.02 μg/L.

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. Applying *Sulfurospirillum halorespirans* and *Dehalococcoides* sp. communities for biodegradation of TCE in groundwater, 95% removal efficiency was achieved and as by-products vinyl-chloride and ethane were detected [7]. Ozonization combined with γ–radiation was also successfully applied to remove TCE from drinking water with an efficiency of 98% [8]. 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 [9–11]. 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 [12–14]. The applicability of ferrate for removal of heavy metals [15], cyanide [16], hydrogen sulfide [17], ammonia [18], arsenic [19] or organic contaminants e.g. bisphenol-A [20], carbohydrates [21], phenol and chlorophenols [22], pharmaceutical residues [23], personal care products [24] or for reduction of TOC content of biologically treated wastewater [25] was demonstrated in the literature. It should be emphasized that the removal efficiencies highly depended 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 aqueous solutions. In a pioneer work the TCE removal

* Corresponding author. Tel.: +36 13722607.
  E-mail address: zaray@chem.elte.hu (G. Záray).

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 was investigated [26]. At FeO_4^{2-}/TCE molar ratio of 182:1, the ferrate oxidation–coagulation processes followed by gas (N_2) flocculation resulted in practically a full removal of TCE. However, it should be noted, that during the gas flocculation a considerable amount of TCE could be volatilized. The influence of pH on the degradation of TCE was also studied applying potassium ferrate in the K_2FeO_4/TCE molar ratio range of 1:1 to 9:1 [22]. It was established that the extent of TCE degradation in model solution achieved its maximum at pH 8, and about 85% of TCE was removed at molar ratio of 9:1. The lower degradation of TCE in the moderately acidic pH range, where the oxidation potential of the ferrate is high, was explained by the higher rate of aqueous ferrate decomposition than the rate of ferrate reaction with TCE.

TCE degradation was investigated also in model solutions applying electrochemically generated ferrate at various pH values [27]. According to 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 with a treatment time of 30 min. As intermediate products ethyl chloride, dichloroethylene, chloroform, 1,1-dichloropropene, trichloroacetic acid, trichloroethane, and as end-product Cl^- were identified. On basis of these three papers focused on model solutions it can be expected that the oxidation of this non-dissociating contaminant especially in presence of groundwater matrix needs a relatively high ferrate/TCE molar ratio to achieve an efficient degradation.

In this work TCE removal from model solutions and groundwater obtained from a chlorinated hydrocarbons contaminated area and spiked in the laboratory, 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. TCE was purchased from Sigma Aldrich Ltd., Hungary, and for its dissolution ultrapure water was used that was produced by Milli Q Plus equipment. Potassium ferrate solution was produced by electrochemical process in our laboratory by using a method similar to that described by Macova et al. [28]. 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 TCE. 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 Section 2.4. 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 cm³ of each water sample was transferred into a septum sealed vial with a volume of 20 cm³.

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 high purity (99.9999%) helium as carrier gas (flow rate 2 ml/min). The temperature of manifold, filament and transfer line was 40 °C, 200 °C, and 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 the liquid phase the sample was thermostated at 40 °C for 1 min and 1 cm³ vapor sample was injected to the GC–MS system. Column temperature program started at 60 °C maintained for 6 min, then ramped at 10 °C/min up to 100 °C (total elution time was 10 min). 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 min, then directly injected to the GC–MS port. Between each measurements the SPME fiber was conditioned at 250 °C for 5 min. GC–MS temperature program started at 40 °C maintained for 0.75 min, 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. [29] Organic hydrocarbon content of the groundwater was identified according to HS/GC–MS method as mentioned in Section 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 amounts of ferrate solution were 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 min. After 1 min stabilization time the TCE concentration was measured in the vapor phase by HS–GC–MS. Prior to the TCE determination in the liquid phase by SPME–GC–MS method the Fe(III) compounds formed during ferrate(VI) reduction were allowed to settle for 15 min. In all cases three parallel measurements were carried out.

Table 1
Physical–chemical parameters of groundwater.

Total inorganic carbon (mg/L)	91.7
Total organic carbon (mg/L)	28.0
Total nitrogen (mg/L)	4.5
pH	8.16
Specific electric conductivity (µS/cm, 20 °C)	1034

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, and 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 Section 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 Section 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 in the range of 10–50 mg/L had only moderate influence on the TCE removal in the pH range 5–9.

However, at pH = 3 and 11, wherein the ferrate is instable or even stabilized, respectively, the removal efficiency of TCE was relatively low. Considering these results all further ferrate treatments were carried out at pH = 7.
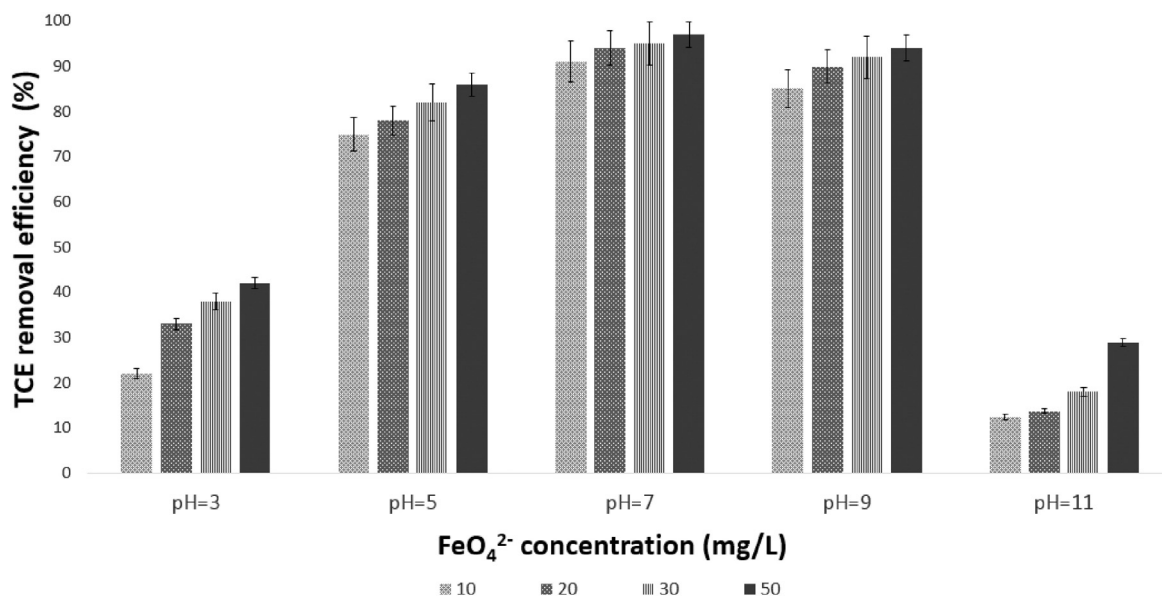
3.3. TCE removal from model solutions

Model solutions having 0.1 and 1.0 mg/L TCE initial concentrations were prepared as mentioned in Section 2.2, and treated by ferrate at concentration of 10, 20, 30 and 50 mg/L applying intensive magnetic stirring for 30 min at pH = 7. After the oxidation process TCE residues were measured both in the vapor and in the liquid phase. The removal efficiency values obtained by the HS–GC–MS and SPME–GC–MS methods are illustrated in Fig 2. These analytical data demonstrate the excellent analytical features of the HS and SPME sampling procedures for determination of TCE. The deviations between the analytical data change in the range of 1%–7%. Removal efficiencies of 96%–97% were measured at 20 mg/L ferrate and 0.1 mg/L TCE concentrations (molar ratio ~200). At ten times higher TCE concentration (molar ratio ~20) the removal efficiencies decreased to 62%–64%. The changing of molar ratio from 20 to 50 resulted in an increment of TCE removal to 73%–74%.

3.4. TCE removal from groundwater

After chemical analysis and filtration of groundwater as mentioned in Section 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 residual TCE were measured both in the vapor and in the liquid phases. The analytical results are presented in Fig 3.

It can be seen that in presence of organic matrix compounds (TOC 28 mg/L) the TCE removal considerably decreased at the same FeO_4^{2-}/TCE molar ratios. Results demonstrate that for groundwater samples having 0.1 mg/L initial TCE concentration, and treated with 50 mg/L ferrate only 41%–42% removal efficiency was achieved. Applying one magnitude higher TCE concentration and using the same operating conditions the TCE removal efficiency decreased to 35%–38%. It can be also concluded that similarly to treatment of model solutions the vapor and liquid phase measurements also correlated with each other.

Fig. 1. TCE removal efficiencies determined for model solution containing TCE in concentration of 0.1 mg/L at various pH and ferrate dosages; analytical data were measured by HS–GC–MS.
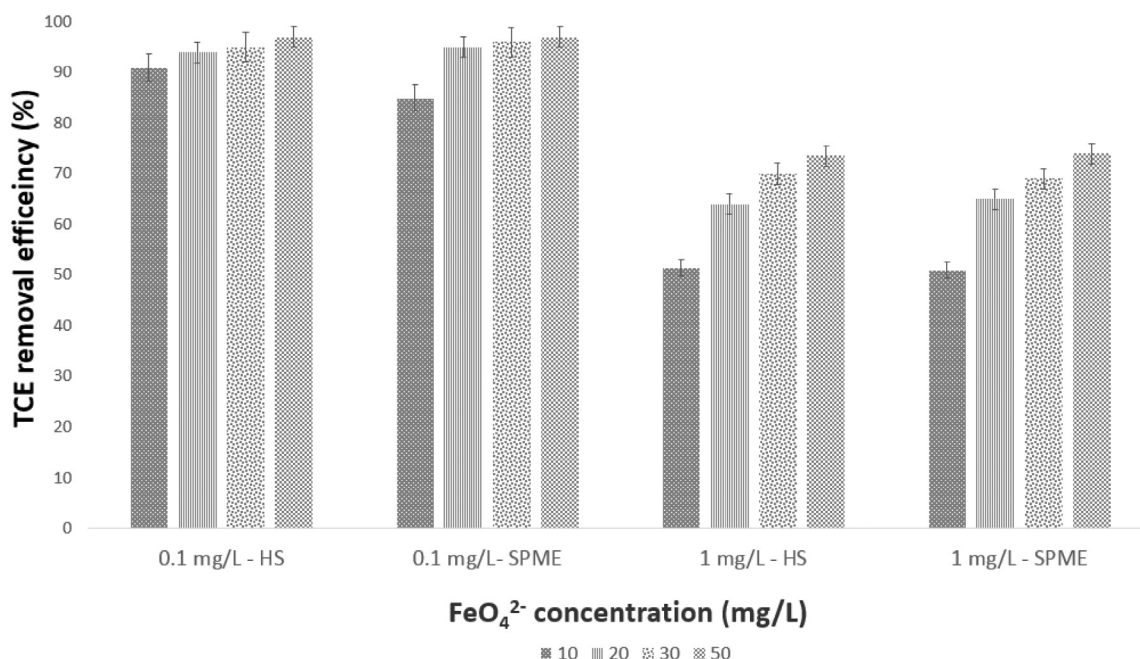
Fig. 2. TCE removal efficiencies for model solutions having 0.1 and 1.0 mg/L initial TCE concentrations at pH = 7 and various ferrate dosages; analytical data were measured by both HS–GC–MS and SPME–GC–MS methods.

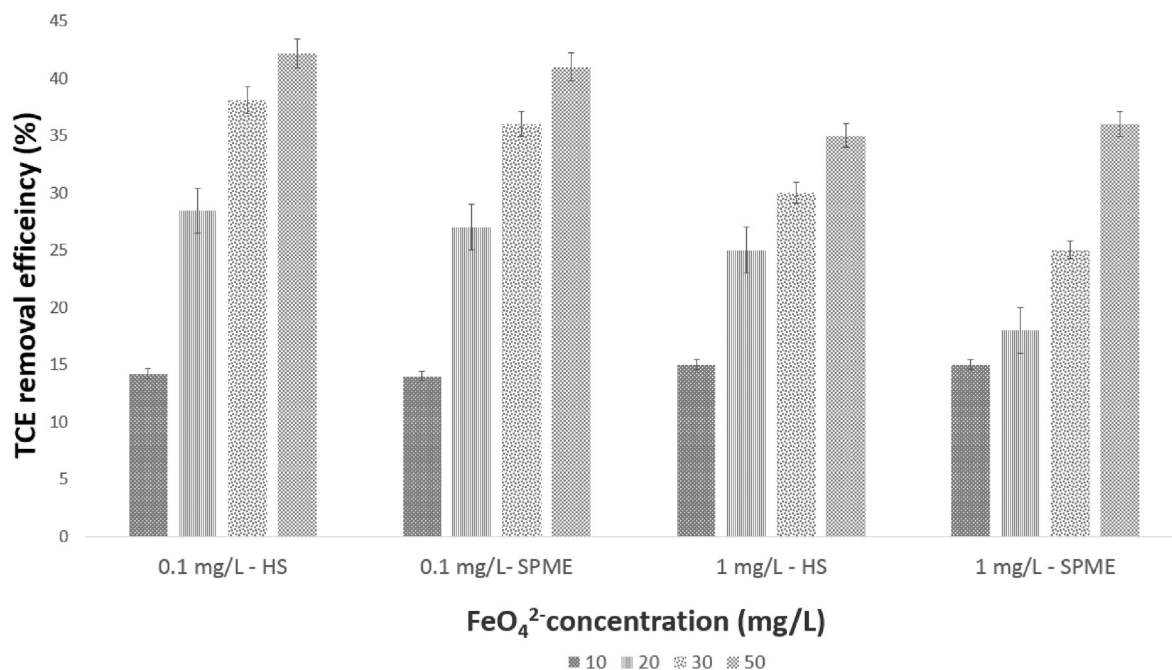### 3.5. Comparing TCE removal efficiencies obtained for model solutions and spiked groundwater

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 at the same ferrate dosage. 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 complex in the 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 helps to estimate the appropriate FeO_4^{2-}/TCE ratio to be applied.

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

Fig. 3. TCE removal efficiencies for 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.
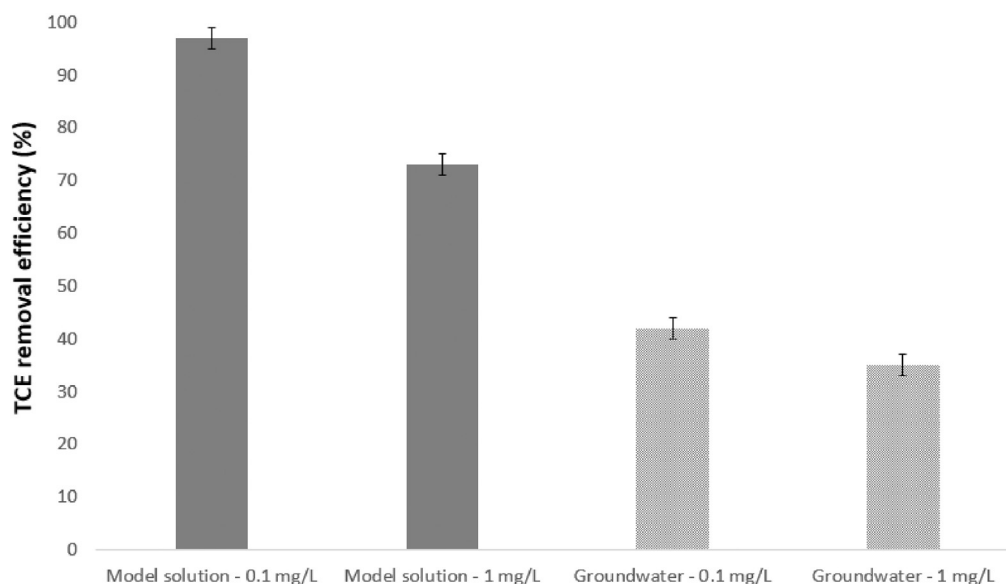
Fig. 4. TCE removal efficiencies for model solutions and spiked groundwater at pH = 7 and ferrate concentration of 50 mg/L measured by HS–GC–MS.

groundwater samples. Comparing the TCE removal from these water samples it can be concluded that the organic groundwater matrix considerably hampers the degradation of TCE 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 and for field experiments suitable groundwater treatment technology, in the next step the chlorine containing by-products will be identified and the chlorine balance will be calculated.

References

[1] F. Aulenta, A. Bianchi, M. Majone, P.M. Papini, M. Potalivo, V. Tandoi, Assessment of natural or enhanced in situ bioremediation at a chlorinated solvent-contaminated aquifer in Italy: a microcosm study, Environ. Int. 31 (2005) 185–190.
[2] E.F. Löffler, A.E. Edward, Harnessing microbial activities for environmental cleanup, Curr. Opin. Biotechnol. 17 (2006) 274–284.
[3] D.J. Munch, D.P. Hautman, USEPA 551.1 Determination of Chlorination Disinfections Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid–Liquid Extraction and Gas Chromatography With Electron Capture Detector, 1995.
[4] D.S. Brown, M.A. Dixon, V.J. Bruckner, G.M. Bartlett, A validated GC–MS assay for the quantitation of trichloroethylene (TCE) from drinking water, Int. J. Environ. An. Ch. 83 (2003) 427–432.
[5] G. Peccorino, L. Scalici, G. Avellone, L. Ceraulo, R. Favara, G.E. Candela, C.M. Provenzana, C. Scaletta, Distribution of volatile organic compounds in Sicilian groundwaters analyzed by head space-solid phase micro extraction coupled with gas chromatography mass spectrometry (SPME/GC/MS), Water Res. 42 (2008) 3563–3577.
[6] A. Gonzalo-Lara, E.J. Sánchez-Uría, E. Segovia-García, A. Sanz-Medel, Critical comparison of automated purge and trap and solid-phase microextraction for routine determination of volatile organic compounds in drinking waters by GC–MS, Talanta 74 (2008) 1455–1462.
[7] É. Mészáros, R. Sipos, R. Pál, Cs Romcsis, K. Márialigeti, Stimulation of trichloroethene biodegradation in anaerobic three-phase microcosm, Int. Biodeter. Biodegr. 84 (2013) 126–133.
[8] P. Gehringer, E. Proksch, W. Szinowatz, H. Eshweiler, Decomposition of trichloroethylene and tetrachloroethylene in drinking water by a combined radiation/ozone treatment, Water Res. 22 (1998) 645–646.
[9] C. Liang, J.C. Bruell, C.M. Marley, L.K. Sperry, Thermally activated persulfate oxidation of trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) in aqueous systems and soil slurries, Soil Sediment Contam. 2 (2003) 207–228.
[10] C. Liang, J.C. Bruell, C.M. Marley, L.K. Sperry, Persulfate oxidation for in situ remediation of TCE I. Activated by ferrous ion with and without a persulfate–thiosulfate redox couple, Chemosphere 55 (2004) 1213–1223.
[11] C. Liang, J.C. Bruell, C.M. Marley, L.K. Sperry, Persulfate oxidation for in situ remediation of TCE II. Activated by chelated ferrous ion, Chemosphere 55 (2004) 1225–1233.
[12] J.Q. Jiang, B. Lloyd, Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment, Water Res. 36 (2002) 1397–1408.
[13] Y. Lee, M. Cho, Y.J. Kim, J. Yoon, Chemistry of ferrate (Fe(VI)) in aqueous solution and its applications as a green chemical, J. Environ. Sci. Health A 10 (2004) 161–171.
[14] J.Q. Jiang, Research progress in the use of ferrate(VI) for the environmental remediation, J. Hazard. Mater. 146 (2007) 617–623.
[15] M. Lim, M.J. Kim, Effectiveness of potassium ferrate (K_2FeO_4) for simultaneous removal of heavy metals and natural organic maters from river water, Water Air Soil Pollut. 211 (2010) 313–322.
[16] S.M. Lee, D. Tiwari, Application of ferrate in the treatment of industrial wastes containing metal-complexed cyanides: a green treatment, J. Environ. Sci. 21 (2009) 1347–1352.
[17] V.K. Sharma, O.J. Smith, F.J. Millero, Ferrate(VI) oxidation of hydrogen sulfide, Environ. Sci. Technol. 31 (1997) 2486–2491.
[18] V.K. Sharma, T.J. Bloom, V.N. Joshi, Oxidation of ammonia by ferrate(VI), J. Environ. Sci. Health A 33 (1998) 635–650.
[19] Y. Lee, H.I. Um, J. Yoon, Arsenic(III) oxidation by iron(VI) ferrate and subsequent removal of arsenic(V) by iron(III) coagulation, Environ. Sci. Technol. 37 (2003) 5750–5756.
[20] C. Li, X.Z. Li, N. Graham, N.Y. Gao, The aqueous degradation of bisphenol A and steroid estrogens by ferrate, Water Res. 42 (2008) 109–120.
[21] V.K. Sharma, M. Sohn, K.A.G. Anquandah, N. Nesnas, Kinetics of the oxidation of sucralose and related carbohydrates by ferrate(VI), Chemosphere 87 (2012) 644–648.
[22] N. Graham, C.C. Jiang, X.Z. Li, J.Q. Jiang, J. Ma, The influence of pH on the degradation of phenol and chlorophenols by potassium ferrate, Chemosphere 56 (2004) 949–956.
[23] V.K. Sharma, K.S. Mishra, Ferrate(VI) oxidation of ibuprofen: a kinetic study, Environ. Chem. Lett. 3 (2006) 182–185.
[24] B. Yang, B.B. Ying, J.L. Zhao, S. Liu, J.L. Zhou, F. Chen, Removal of selected endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs) during ferrate(VI) treatment of secondary wastewater effluents, Water Res. 46 (2012) 2194–2204.
[25] E. Gombos, K. Barkács, T. Felföldi, Cs Vértes, M. Makó, G. Palkó, G. Záray, Removal of organic matters in wastewater treatment by ferrate(VI)-technology, Microchem. J. 107 (2013) 115–120.
[26] J.S. DeLuca, C.A. Chao, M. Asce, C. Smallwood, F. Asce, Removal of organic priority pollutants by oxidation–coagulation, J. Environ. Eng. 109 (1983) 36–46.
[27] J.H. Nam, B.H. Kwon, I.K. Kim, Degradation of trichloroethylene in aqueous phase by electrochemical ferrate(VI), J. Korean Soc. Water Wastew. 26 (2012) 453–461.
[28] Z. Macova, K. Bouzek, The influence of electrolyte composition on electrochemical ferrate(VI) synthesis. part III: anodic dissolution kinetics of a white cast iron anode rich in iron carbide, J. Appl. Electrochem. 42 (2012) 615–626.
[29] APHA, AWWA, WEF Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association, Washington, DC, 2005.