



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

Article history:

Received 8 February 2016

Accepted 11 February 2016

Available online 22 February 2016

Keywords:

Groundwater

Ferrate

Trichloroethylene

Oxidative treatment

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 NaHCO_3 , 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 cm^3 of each water sample was transferred into a septum sealed vial with a 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 \times 0.25 mm, $\text{df} = 1 \mu\text{m}$) using high purity (99.9999%) helium as carrier gas (flow rate 2 ml/min). The temperature of manifold, filament and transfer line was 40 $^\circ\text{C}$, 200 $^\circ\text{C}$, and 220 $^\circ\text{C}$, 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 $^\circ\text{C}$ for 1 min and 1 cm^3 vapor sample was injected to the GC–MS system. Column temperature program started at 60 $^\circ\text{C}$ maintained for 6 min, then ramped at 10 $^\circ\text{C}/\text{min}$ up to 100 $^\circ\text{C}$ (total elution time was 10 min). Injector temperature and split ratio were 250 $^\circ\text{C}$ 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 $^\circ\text{C}$ for 30 min. After that the SPME fiber was introduced into the septum sealed vial containing 10 cm^3 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 $^\circ\text{C}$ for 5 min. GC–MS temperature program started at 40 $^\circ\text{C}$ maintained for 0.75 min, then ramped at 20 $^\circ\text{C}/\text{min}$ up to 160 $^\circ\text{C}$ (total elution time was 6.75 min). Injector temperature was 230 $^\circ\text{C}$ 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 cm^3 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.

Download English Version:

<https://daneshyari.com/en/article/1227502>

Download Persian Version:

<https://daneshyari.com/article/1227502>

[Daneshyari.com](https://daneshyari.com)