Laboratory scale study for remediation of polluted groundwater by ferrate treatment

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1. Introduction

During the last two decades the removal of different organic molecules from water matrices by ferrate treatment was widely studied first of all in laboratory scale trials. Mostly one organic compound was reacted with ferrate and the decomposition of parent molecules were measured in the function of pH at different contaminant/ferrate molar ratios. For example phenol [1], chlorophenols [2,3], trichloroethylene [4,5], secondary alcohols [6], amino acids [7], carboxylic acids [8], carbohydrates [9], amines [10] and different pharmaceuticals such as ibuprofen, diclofenac, β-lactam, and fluoroquinolone [11–14] were investigated. Sharma in his review discussed the kinetics and mechanism of ferrate oxidation of different organic compounds [15]. This is extremely useful for calculation of expected by-products which can be less or even more toxic than the parent molecules. However, in case of environmental remediation (e.g. waste or groundwater treatments) several organic compounds with different chemical structure, dissociation ability and reactivity are simultaneously present and their removal efficiencies and the final oxidation products can be not estimated.

To develop ferrate technology for environmental remediation (e.g. field experiment for purification of contaminated groundwater) it is necessary to produce the ferrate solution on-site in order to eliminate the limitations caused by decomposition of ferrate during the transfer and storage. For this technological development the electrochemical production of liquid ferrate offers the most promising way. In 2001 Licht [16] patented the first online electrochemical formation of ferrate(VI) for water treatment. Later Yu and Licht [17] reported the advances of the electrochemical Fe(VI) synthesis. Macova et al. [18] in their review summarized the technological parameters influencing the efficiency of electrochemical ferrate(VI) production using either a dissolving iron anode in highly alkali solution [19–27] or an inert electrode in Fe(III) solution [28,29]. In case of the latter one only three electrons are necessary to achieve the required +6 iron oxidation state, thus only half of the electrical charge is required. However, there are considerable limiting factors e.g. the low stability of ferrate(VI) formed in solution containing Fe(III) ions and the low solubility of iron species in the anolyte solution. Due to these disadvantages of "inert electrode in Fe(III) solution" system and the well documented research data of the dissolving iron anode technology (e.g. the influence of electrolyte temperature and composition, geometry and composition of anode, and activation of anode surface on the efficiency of ferrate(VI) production) the dissolving iron anode technology was selected for pilot scale trials. Jiang et al. [30] applied the electrochemically online generated ferrate(VI) for sewage treatment. The sewage flow rate was kept constantly as 2 m³/h. Using the online generated ferrate(VI) at concentration of 0.03 mg/L as Fe^{6+}, it was possible to reduce the 1125 mg/L COD value by 50°% and simultaneously the concentration of suspended solids and phosphate decreased by 79 and 56%, respectively. In three years later Jiang et al. [31] reported on a full scale trial, where the modified ferrate reactor operated automatically for continuous 24 h run. Due to the high current efficiency (60–65%) the ferrate concentration could reach to 538 mg/L as Fe^{6+}, which is higher than that gained from the pilot scale production trials. Recently Gonzales-Merchan et al. [32] studied the effect of ferrate on degradation of thiocyanates and ammonia in gold mine effluent applying ferrate in concentration of 50–500 mg/L. In framework of a

laboratory scale experiment the authors demonstrated that the SCN^- in concentration of 470 $\pm$ 70 mg/L were efficiently degraded (<97%), however, the removal of NH_3-N needs a longer treatment time than 1 h or a complementary technology such as nitrification-denitrification is required. These publications indicate that the research interest slowly turned to the real environmental problems (e.g. treatment of industrial or communal wastewater) and on basis of laboratory scale experiments more and more pilot or industrial scale technology will be developed.

In this paper the results of a laboratory scale experiment focused on the ferrate treatment of highly contaminated groundwater (COD 4050 $\pm$ 142 mg/L) were presented. The degradation rates of 44 organic contaminants were determined by head-space gas chromatograph mass spectrometer system. These experimental data form the basis of an industrial scale technology applying on-site produced ferrate solution.

2. Materials and methods

2.1. Sampling and chemicals

The groundwater was freshly sampled by pump from an observing well located in a contaminated industrial area and filled into glass containers. Then the samples were transported to the laboratory. Where the sodium ferrate solution with concentration of 6–8 g/L was produced by our electrochemical method (under patent procedure). The accurate ferrate concentration of the freshly prepared solution was determined by spectrophotometry measuring the absorption of ferrate at 505 nm. For pH adjustment 2 M sulfuric acid (analytic grade, Merck, Germany) was used.

2.2. Analytical instrument and methods

The COD values were measured by standard procedure [33] using $K_2Cr_2O_7$. The pH was measured by a Jenway 3510 equipment. Volatile compounds were determined by headspace-gas chromatograph–mass spectrometer (HS/GC–MS). For analysis of halogenated aliphatic and aromatic hydrocarbons a Bruker Scion 436 GC–MS system equipped with SHS-40 headspace autosampler and BR-5 column (30 m × 0.25 mm, df 1 μm) was used applying high purity helium (99.9999%) as carrier gas (2 mL/min) and selective ion monitoring (SIM). Another equipment (Agilent 7890 GC and Agilent 597 SC MS) equipped with capillary column Restek Rxi-624 Sil MS (61 m × 0.32 × 1.2 μm) was used for measurement of aliphatic alcohols, ethers, ketones and esters. The operating conditions are listed in Table 1.

Table 1
Operating conditions of GC–MS equipments for determination of halogenated aliphatic and aromatic hydrocarbons as well as ethers, esthers and ketones.

Parameters	Halogantd aliphatic and aromatic hydrocarbons (HAHC)	Aliphatic alcohols, ethers, esthers and ketones
Sample preparation/time of thermostat	80 °C	80 °C
Sample preparation/temperature of thermostat	10 min	10 min
Injector temperature	250 °C	200 °C
Split ratio	33:1	30:1
Temperature program of the capillary column oven	37 °C hold 10 min	37 °C hold 6 min
	5 °C/min to 62 °C → hold 1 min	20 °C/min to 70 °C → hold 3 min
	5 °C/min to 102 °C → hold 1 min	20 °C/min to 80 °C → hold 2 min
	25 °C/min to 250 °C → hold 1 min	20 °C/min to 200 °C
Transfer line temperature	250 °C	200 °C
Ion source temperature	200 °C	230 °C

2.3. Ferrate treatment

One liter freshly sampled groundwater was filled into septum sealed glass flasks with volume of 1.3 L. Following the measurement of ferrate concentration of the freshly produced sodium ferrate solution (6–8 g/L), the calculated amounts of ferrate solution were added to the groundwater samples by using an injection syringe. In order to adjust the pH value of alkalic solution to 7 calculated amounts of 2 M sulfuric acid were added to the samples on similar way. During the treatment the water samples were agitated by Teflon coated magnetic stirrer bars for 5 or 30 min. After this first treatment step 20 mL solution was removed from the septum sealed flasks for the measurement of COD and identified organic volatile contaminants. In the second and the third step the calculated amounts of ferrate solution and sulfuric acid were added again at the same way as mentioned above and after the treatment steps 20 mL solution was removed for COD and HS/GS-MS measurements Before the analytical investigations the iron-hydroxide was separated by centrifugation for 1 min at 3500 rpm. In all cases three groundwater samples were simultaneously treated and characterized by analytical measurements.

Table 2
Mean concentration of 44 organic contaminants in the groundwater before and after the ferrate treatment determined by HS/GC–MS.

| Compounds	Mean concentration (μg/L)		Degradation rate (%)
	Before ferrate treatment	After ferrate treatment	
Isopropyl-alcohol	1,080,080	320,276	70
Acetone	415,574	131,795	68
Methanol	392,104	145,542	63
Ethanol	170,207	39,192	77
Chlorobenzene	62,810	19,066	70
1,2-Dichloroethane	49,548	20,577	59
Toluene	42,979	7424	83
Benzene	4908	3418	30
Isobutanol	4902	1643	67
m-Xylene	4621	317	93
Diethyl-ether	4277	505	88
Methylene chloride	3308	838	75
2-Chloroethanol	2973	n.d.	100
Carbontetrachloride	2603	101	96
Chloroform	2227	244	89
Ethyl acetate	1833	n.d.	100
Ethyl benzene	1692	119	93
Tetrahydrofuran	1611	283	82
n-Butanol	1472	295	80
p-Xylene	1428	123	91
Methyl-isobuthyl-ketone	1155	178	85
Trichloroethylene	813	62	92
2-Butanol	775	171	78
o-Xylene	733	64	91
Vinyl-chloride	469	24	95
1,1,2-Trichlororethane	423	n.d.	100
t-Butanol	393	89	78
1,4-Dichlorobenzene	175	16	91
1,2-Dichlorobenzene	67	7.7	89
1,2-Dichloropropane	41	6.7	84
Tetrachloroethylene	39	1.7	96
2-Pentanone	38	30	23
1,1,2,2-Tetrachloroethane	26	n.d.	100
1,3,5-Trimethyl-benzene	18	0.2	99
n-Propyl-benzene	16	0.1	99
1,2-Dichloroethylene	9.9	1.7	83
1,3-Dichlorobenzene	6.6	0.6	91
1,2,4-Trimethyl-benzene	5.4	0.3	94
Tribromomethane	3.5	n.d.	100
i-Propyl-toluene	3.4	0.2	94
p-Ethyl-toluene	2.8	0.3	89
1,2,3-Trimethyl-benzene	2.8	0.2	93
o-Ethyl-toluene	1.8	0.3	83
m-Ethyl-toluene	1.2	0.1	92

n.d. = not detected.
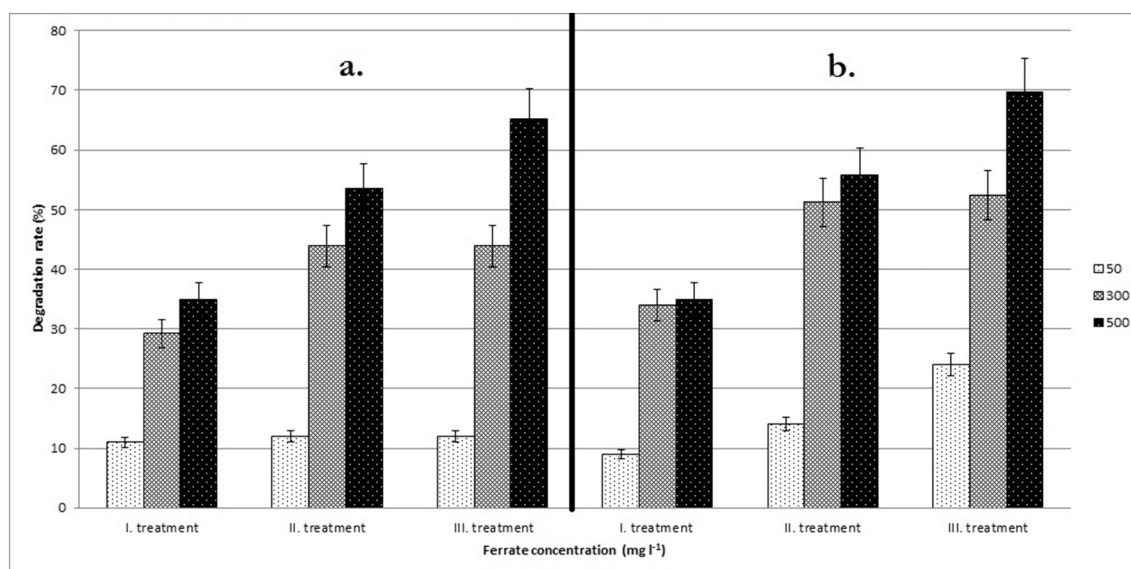
Fig. 1. Change of chemical oxygen demand during the 3-steps ferrate treatment of groundwater applying 50, 300 and 500 mg/L ferrate concentration and 5 or 30 min treatment time.

3. Results and discussion

3.1. Characterization of groundwater to be treated

The COD values amounted to 4050 ± 142 mg/L 44 organic compounds were identified and quantified by HS/GC–MS method characterized in Section 2.2. The concentration values of organic contaminants are listed in Table 2. It can be seen that the main contaminants were aliphatic alcohols, first of all isopropyl-alcohol with concentration of 1.08 g/L, furthermore methanol and ethanol were also dominant with concentration of 0.39 and 0.17 g/L, respectively. Acetone had the second highest concentration of 0.41 g/L. In addition to these main contaminants 17 halogenated aliphatic and aromatic hydrocarbons, as well as 15 aromatic hydrocarbons were present in the groundwater in total concentration of 125.2 mg/L and 56.4 mg/L, respectively.

3.2. Change of the COD and the sum of concentrations of 44 organic compounds measured by HS/GC–MS after the ferrate treatment steps

Fig. 1 demonstrates the reduction of COD values after the treatment steps applying ferrate concentration of 50, 300 and 500 mg/L and treatment time of 5 (a) and 30 min (b). On basis of these results the following statements can be done:

• The COD values decreased in all treatment steps with increasing concentration of ferrate, however, the efficiency of ferrate treatment decreased during the consecutive treatment steps. For example at 500 mg/L ferrate concentration and 5 min treatment time, after the first, second and third treatments 35, 19 and 11% degradation rates were determined, respectively. It means the concentration of by ferrate-degradable organic compounds decreased.
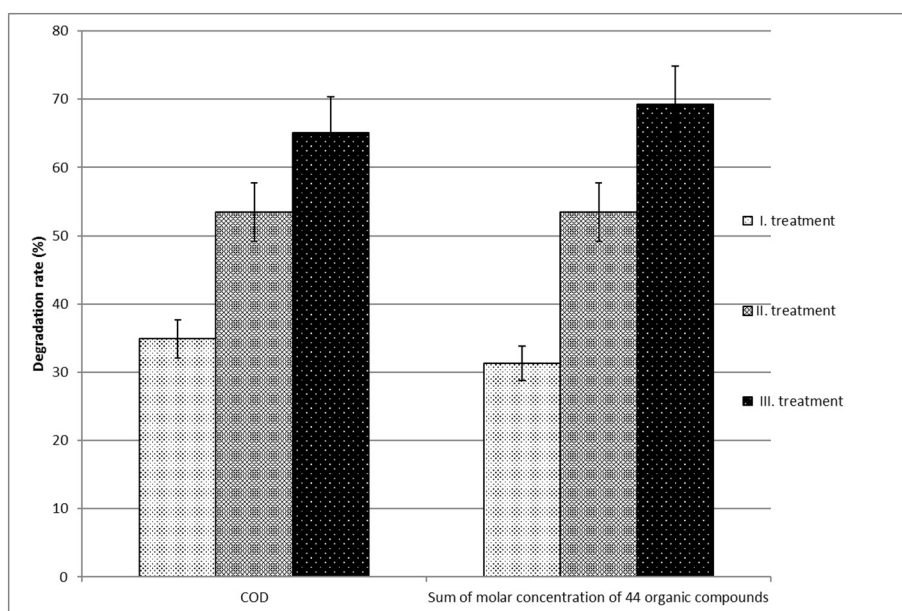

Fig. 2. Relative change of chemical oxygen demand and the sum of molar concentrations of 44 volatile organic compounds after the 3-step ferrate treatment applying 500 mg/L ferrate concentration and treatment time of 5 and 30 min.
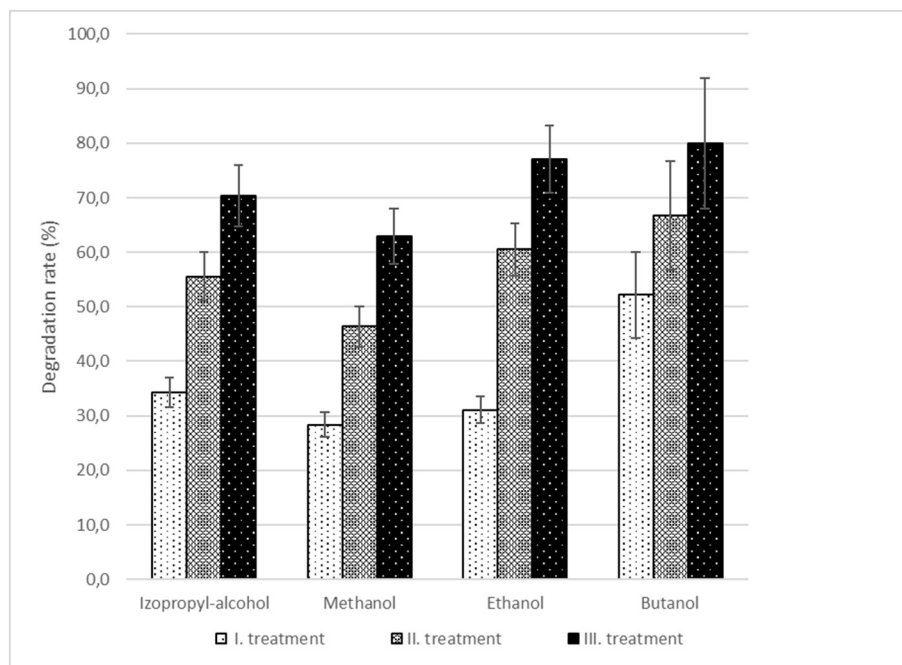
Fig. 3. Degradation rates of the main aliphatic alcohol contaminants after the 3-step ferrate treatment applying 500 mg/L ferrate dosage and 5 min treatment time.

• The longer treatment time resulted in only a moderate increment in the reduction of COD values. Therefore from technological and economical points of view the 5 min treatment time was selected for the further experiments and it can also be recommended for the remediation technology.

3.3. Reduction of COD and molar concentration of contaminants

Comparing the changes of COD and the sum of molar concentration of 44 identified and quantified organic contaminants, similar trend can be observed (Fig. 2). However, due to the formation of non-volatile degradation compounds the reduction of COD value falls behind the concentration change of parent volatile molecules. Since the different groups of organic compounds with different chemical structure and substituents have different degradability by ferrate, selected target molecule groups (aliphatic alcohols, chlorobenzenes, xylenes and trimethylbenzene compounds) were separately studied. The removal efficiency values obtained by the 3-steps treatment at 500 mg/L ferrate concentration and treatment time of 5 min for the four different molecule groups are demonstrated in Figs. 3–6. Among the four aliphatic alcohols investigated, methanol was the less degradable compound and with increasing length of carbon chain the removal efficiency values increased (Fig. 3). In case of butanol about 80% removal was measured. However, due to the position of hydroxyl group in the isopropyl-alcohol molecule its nucleofil character is less than those of ethanol, therefore their degradation rate reached only 70% localizing between the methanol (63%) and ethanol (77%).

The degradation of mono-chlorobenzene and the dichlorobenzene isomers in model solutions and in presence of groundwater matrix was recently studied by our group applying 50 mg/L ferrate concentration and molar ratios of 200–500 [34]. During this experiment the 1,2 dichlorobenzene isomer had the highest and the mono-chlorobenzene the lowest degradation rate. In the present experiment at 10 times
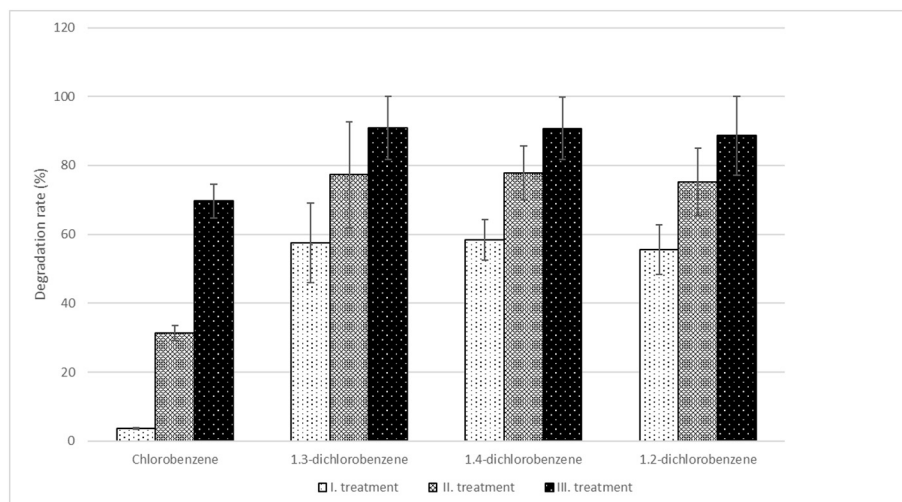

Fig. 4. Degradation rates of chlorobenzenes after the 3-step ferrate treatment applying 500 mg/L ferrate dosage and 5 min treatment time.
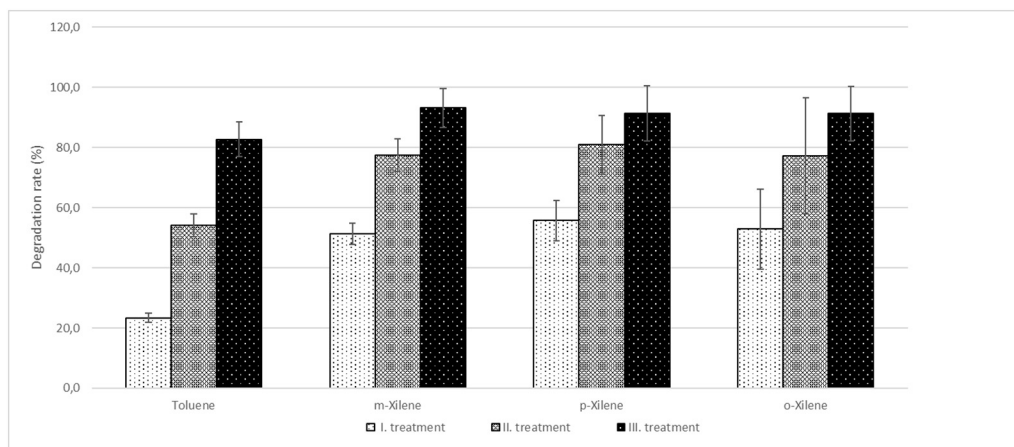
Fig. 5. Degradation rates of toluene and xylene compounds after the 3-step ferrate treatment applying 500 mg/L ferrate dosage and 5 min treatment time.
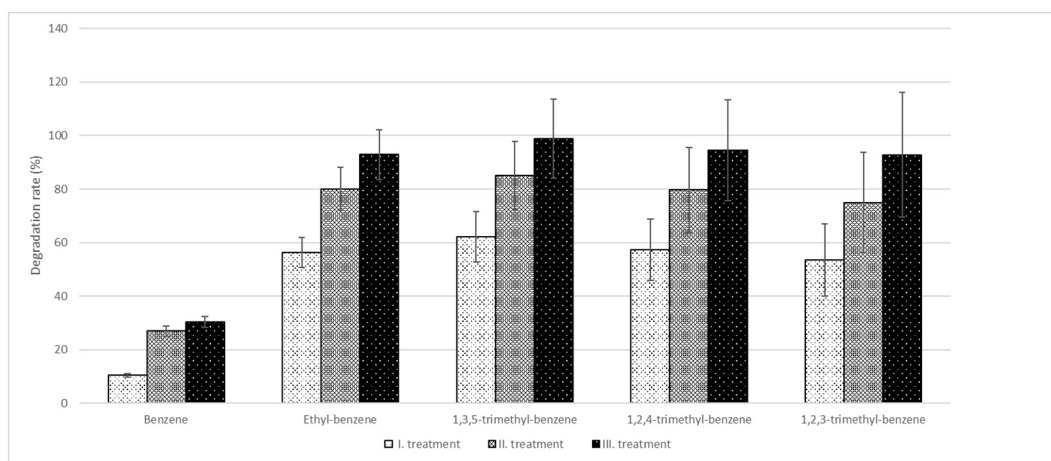

Fig. 6. Degradation rates of benzene, ethyl-benzene, trimethyl-benzene compounds after the 3-step ferrate treatment applying 500 mg/L ferrate dosage and 5 min treatment time.

higher ferrate concentration (500 mg/L) and in presence of a more complicated matrix, all three dichlorobenzene isomers had practically the same high degradation (>90%), however, the mono-chlorobenzene showed again the lowest degradability (Fig. 4).

Similar phenomenon can be observed in case of toluol and xylene isomers. It means toluol showed the lowest degradation (82%) and the three xylene isomers had higher (92–93%) but practically the same degradation rate (Fig. 5). If three methyl groups are substituted on the aromatic ring, the degradation of parent isomers became a little higher (Fig. 6). The increasing number of methyl groups on the aromatic ring resulted in the following degradation order: benzene 30%, toluene 82%, xylenes >90%, and trimethylbenzenes >95%.

4. Conclusion

The simultaneous degradation of different organic contaminant in groundwater can be realized by addition of freshly prepared, electrochemically produced ferrate solution into the contaminated groundwater and its rapid distribution by mixing. In case of highly contaminated groundwater (COD value > 1000 mg O_2/L) a multistep ferrate treatment is necessary to achieve an efficient degradation of parent molecules and simultaneous reduction of the COD value below the prescribed limit value. Considering the costs and the time demand of a multistep procedure, it would be useful to rather investigate the application of a posttreatment of the ferrate treated groundwater using granulated or powdered active carbon. In the next laboratory scale experiment such post-

treatment will be coupled with two- or three-step ferrate treatment technology and the by-products in the solution phase will be identified prior to the planned pilot scale trials.

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