BTO 2014.205s | Maart 2014

BTO rapport

The use of ferrate for oxidation and disinfection

KWR Watercycle Research Institute

BTO

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BTO 2014.205s | Maart 2014

Opdrachtnummer
B222001-030

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Verzonden aan
Dit rapport is verspreid onder BTO-participanten. Een jaar na publicatie is het openbaar.

Jaar van publicatie
2014

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Abstract

Ferrate (iron IV, V and VI) is known to be a very efficient oxidant. Upon reduction the iron is turned into Fe(III), which in water treatment often is used as a coagulant. Thus, theoretically by adding ferrate to water two goals can be met: oxidation of organic micropollutants and coagulation. At KWR a few years ago experiments were carried out with ferrate to check whether ferrate is a promising material for drinking water treatment. However, it was found that ferrate was not stable enough for practical applications, certainly not on a large scale. For such processes it would be necessary to have a ferrate solution that can be dosed to the water and is stable for several days. In the meantime, processes have been optimized and there is some literature on more stable ferrate. Prof. V. Sharma of the Center of Ferrate Excellence (Florida Institute of Technology) provided us with some samples: one containing commercial Fe(V), one experimental Fe(V) and one experimental Fe(IV). Two sets of experiments were carried out with all three types of ferrate:

Experiments with dissolved ferrate. The ferrate first was dissolved at pH 9, as is described in literature. However, this seemed to result in a violent reaction, with gas evaporation and color changes. Although the solutions obtained were able to oxidize a mixture of pharmaceuticals, conversion was not very high, probably as a result from the relatively low ferrate concentrations (≤ 1mg/L) . The solutions were also not effective for disinfection purposes.

Experiments with solid ferrate. Now a very high conversion of most pharmaceuticals could be obtained, even though concentrations used were lower than in literature (ca. 1 mg/L whereas mostly 5 mg/L is applied). For some compounds, which are very difficult to degrade in other oxidation processes (like metformin in UV/H_2O_2), ferrate appeared to be very effective. Surprisingly, contrary to what is reported in literature, it was found that Fe(IV) was more effective than Fe(V). Possibly this is caused by the higher reactivity and thus lower stability of Fe(V).

Although more research is required, especially to find a way to keep ferrate solutions stable e.g. for use on a large scale, oxidation by ferrate may be a very interesting option.

Contents

1 Introduction

1.1 Advantages of ferrate in drinking water production

In drinking water production often $FeCl_3$ is added as a coagulant as one of the first steps in DWT in order to remove colloidal particles. Furthermore, disinfection plays an important role in drinking water purification. During recent years it has become clear that sources for drinking water contain large numbers of organic micropollutants, in increasing concentrations. This mainly is the case for surface water, but also in ground water more and more micropollutants can be found. There are several ways to deal with such micropollutants. Adsorption by activated carbon in many cases is less effective, as these micropollutants often are relatively small, hydrophilic and sometimes even charged molecules. Membrane filtration is very effective for relatively large molecules, but it has the disadvantage that a concentrate is formed, which has to be dealt with, and that it is an energy intensive process. Oxidation, or advanced oxidation processes can be very effective in converting these micropollutants, which in principle can be mineralized completely (i.e. converted into CO_2 and H_2O). This is very expensive, and thus in most cases they are degraded into small, better biodegradable, compounds. Oxidation processes are becoming more and more important in water treatment.

Ferrate, Fe(V) and Fe(VI) ions, is a very effective oxidant. As it decomposes in water it produces dissolved oxygen, peroxide and hydroxyl radicals. The overall reaction of Fe(VI) in pure water is given by [Jiang and Lloyd, 2002]:

$$4FeO_4^{2-} + 10H_2O \rightarrow 4Fe(OH)_3 + 8OH\cdot + 3O_2$$

Fe(V) and Fe(IV) can yield different final reduced species (Fe(II) or Fe(III) or both Fe(II) and Fe(III) via 1 e- and 2 e- pathways [Sharma, 2013]. In the actual reaction scheme pH also plays a very important role. Both ferrate (VI) and Ferrate(V) have triportonated, deprotonated, monoprotonated, and deprotonated species present in the acidic to basic pH range, and the the reactivity of the organic micropollutants involved also depends upon the charge of the compounds.

The presence of small particles in a solution is expected not to have a large effect on oxidation reactions (contrarily to UV/H_2O_2 processes). Only in case the organic micropollutant has been adsorbed onto the particles it may affect the oxidation efficiency.

During the process Fe(III) is formed, which can be used for coagulation purposes. Besides, from literature [Gijsbertsen, 2004; Jiang, 2013] it is known that this oxidation by ferrate also is very effective in deactivation of microorganisms. Thus, by adding ferrate three processes can be combined: oxidation of organic micropollutants, coagulation by the formed Fe(III) and disinfection. In previous KWR research the possibilities of using ferrate in water treatment was investigated [Gijsbertsen, 2004; Gijsbertsen-Abrahamse et al., 2006; Gijsbertsen and Siegers, 2006]. It was found that ferrate is an effective disinfectant, that it is an efficient coagulant, and a strong oxidizing agent, especially at pH 6-8. However, the ferrate appeared not to be very stable, as a result of which it would be difficult to use in full scale processes. However, during recent years much research has been done on ferrate, and according to literature it now should be possible to have stable ferrate, and it also is commercially available. Thus, it was decided to check whether indeed ferrate now can be handled and kept

stable in an easy way and whether it is possible to use ferrate to convert organic micropollutants like e.g. pharmaceuticals. The results are described in this report.

2 Literature study

2.1 Recent literature on ferrate

As the previous study was carried out in the period 2004-2006, it was decided to focus the present literature study on more recent publications.

In wastewater several oxidants are applied, like chlorine, hypochlorite, chlorine dioxide, ozone, and hydrogen peroxide. Under acidic conditions Fe(VI) has the highest oxidation reduction potential (2.2 V), under alkaline conditions this is reduced to 0.7 V. The main advantage of ferrate is that the oxidation product, Fe(III) is not toxic or harmful, and that it can be used as a coagulant/flocculant in the subsequent treatment process [Gombos et al., 2013]. For the use of ozone extra safety precautions are required, whereas for hydrogen peroxide in UV/H_2O_2 processes always a large excess of peroxide has to be added, which has to be removed afterwards, e.g. by means of filtration over activated carbon. There are three preparation methods for ferrate (VI): wet and dry oxidation and an electro-chemical method (in a concentrated alkali solution of metal hydroxides) [Jiang, 2014]. [Luo et al., 2011] and [Jiang, 2014] describe several methodologies for the analytical determination of ferrate.

In 2006 [Sharma et al, 2006] published an investigation into the oxidation of sulfonamide antimicrobials by ferrate(VI). Complete removal of the sulfonamides was obtained, and the reaction mechanisms were unraveled. Since then ferrate has been studied for disinfection purposes and for the oxidation of pharmaceuticals, endocrine disrupting compounds, andpersonal care products [Jiang, 2014]. [Hu et al., 2009] studied the oxidation of carbamazepine by both Mn(VII) and Fe(VI) in deionized water, and found that oxidation with Fe(VI) is fastest at a pH < 7. It was observed that Fe(VI) oxidizes carbamazepine by means of an electrophilic attack at the olefinic group in the central heterocyclic ring. Subsequently, the Fe(VI) can also react with some of the intermediates formed initially, as a result of which the olefinic double bond in the central heterocyclic ring was transformed into alcohols, aldehydes, ketones and carboxyl groups, while the aromatic rings remained intact. [Lee et al, 2009] applied ferrate for municipal wastewater treatment, aiming at simultaneous micropollutant oxidation and phosphate removal. They selected micropollutants containing electron-rich moieties such as phenol, anilines, amines and olefins in the low μM concentration range. At Fe(VI) doses higher than 5 mg Fe/L they obtained over 85% elimination of the micropollutants. Furthermore, the authors observed that Fe(V) was significantly more reactive than Fe(VI). [Anquandah et al., 2011] studied the oxidation of trimethoprim with Fe(VI), and here too it was found that the oxidation rate increases with decreasing pH. This finding also is in accordance with the findings of [Sharma et al., 2012], when studying the oxidation of sucralose and related carbohydrates by ferrate(VI), and of [Casbeer et al., 2013], describing the kinetics and mechanism of tryptophan oxidation by ferrate(VI). [Anquandah et al., 2013] studied the oxidation kinetics and mechanism for propranolol. In the past few years oxidation by ferrate has been applied to several micropollutants. [Jiang and Zhou, 2013] concluded that ferrate is very effective for the removal of ciprofloxacin, as this compound has electron rich organic moieties in its structure. Contrarily, for ibuprofen, which contains electron-withdrawing groups, only 30% could be removed, at a much slower reaction rate. This also explains why naproxen could be removed for 43% and n-acetyl sulphametoxazole only for 8% under the circumstances applied. [Jiang et al., 2013] concluded that in wastewater ferrate(VI) is capable of removing more than 85% of various micropollutants containing electron rich moieties. The oxidation strongly depends

on pH, not only because of the effect on the ferrate, but also because of the effect of pH on the micropollutants (based on their pKa values). Similar results were obtained by [Sharma et al., 2013], who explained the oxidation of β-lactam antibiotics amoxicillin and ampicillin by ferrate(VI) using acid-base equilibria of both Fe(VI) and the organic molecules. It was concluded that ferrate reacts with the amine moieties of the compounds studied. This is in accordance with the findings of [Jiang 2013], who tested 68 different compounds in wastewater. He observed that ferrate(VI) slowly reacted with acidic pharmaceuticals like ibuprofen, because the carboxylic group is an electron-withdrawing functional group, which can depress the reaction of the aromatic ring with Fe(VI). However, ferrate(VI) was found to efficiently remove several endocrine disrupting chemicals, pharmaceuticals and personal care products (depending on circumstances 50-70% or higher), and appeared to be efficient in inactivating eschericha coli, coliforms and f2 coliphage viruses. [Wilde et al., 2013] used ferrate for the degradation of β-blockers (atenolol, metoprolol and propranolol) in hospital wastewater. They found that all three β-blockers were degraded for over 90%, and that a 60% reduced aromaticity could be achieved.

[Sharma, 2013] studied the kinetics and mechanism of ferrate reactions. He concluded that K_2FeO_4 is stable for long periods of time when stored under dry conditions, but that it decomposes slowly to amorphous Fe(III) hydroxide nanoparticles when exposed to moisture. Both ferrate(V) and ferrate (VI) have triprotonated, deprotonated, monoprotonated and deprotonated species present in the acidic to basic pH range. Ferrate(VI) becomes a stronger oxidant upon protonation. Ferrate(VI) is more basic than ferrate(V). By transfer reactions involving one or two electrons finally Fe(III) is formed. Ferrate(V) and (IV) were found to react much faster than ferrate(VI). In this paper oxidation by ferrate was applied to a mixture of pharmaceuticals, containing carbamazepine, sulfonamide, antimicrobials, trimethoprim, tetracycline, ibuprofen, ciprofloxacin, enrofloxacin, diclofenac, sulfamethoxazole and trimethoprim.

According to [Gombos et al., 2013] Fe(VI) could effectively diminish the reactive phosphate concentration in secondary effluents, and that the AOX concentration increased during Fe(VI) treatment. Furthermore ferrate(VI) was successfully applied to oxidize phenols, anilines, amines and olefins (>85% at concentrations Fe(VI) ≥ 5 mg/L). Increasing the Fe(VI) dose resulted in a higher COD and TOC removal.

3 Experiments

3.1 Ferrate samples used

Via prof. Sharma of the Center of Ferrate Excellence (Florida Institute of Technology) three ferrate samples were obtained. They were made by dr. Libor Machala from the Regional Centre of Advanced Technologies and Materials, Palacký,University in Olomouc Czech Republic:

Table 3-1: composition of iron samples used, as provided by dr. Libor Machala (Regional Centre of Advanced Technologies and Materials, Palacký, University in Olomouc Czech Republic).

Sample	Total wt% Fe	$KFeO_2$	K_3FeO_4	Na_4FeO_4	Active Fe wt%
Commercial sample (Fe(V)	24.52	85.365	14.635	--	3.59
Ferrate (V)	18.89	29.662	70.338	--	13.29
Ferrate (IV)	12.81	34.014	--	65.959	8.45

A full analysis of these samples is shown in appendix I.

3.2 Experiments with dissolved ferrate

Dry ferrate was dissolved in 1 L of a HPO_4/BO_3 buffer solution of pH 9, as described in literature [Luo et al., 2011; Sharma et al., 2012]. Upon addition of the ferrate to the buffer solution in some cases immediate reaction could be observed. Details are given in Table 3-2.

Table 3-2: stock solutions of ferrate samples

Sample	Dry ferrate (g)	Solution (L)	[Fe(V)] or [Fe(IV)] (mg/L)	effect
Commercial Fe(V)	6.7	1	240 Fe(V)	Purple color, gas formation
Fe(IV)	1.7	1	226 Fe(V)	Violent reaction, brown color
Fe(V)	1.42	1	120 Fe(IV)	Purple color, no obvious reaction

9 mL of this stock solution was diluted to 1.8 L for the reactions with pharmaceuticals. The final Fe-concentrations are shown in Table 3-3.

Table 3-3: solutions of ferrate samples

solution	mg /L	pH
1	1.20 commercial Fe(V)	6
2	1.20 commercial Fe(V)	8
3	0.72 Fe(IV)	6
4	0.72 Fe(IV)	8
5	0.94 Fe(V)	6
6	0.94 Fe(V)	8

To these solutions 20 mL of a stock solution containing several pharmaceuticals (concentrations 1 mg/L) was added in 20 L tapwater from the city of Nieuwegein. For most pharmaceuticals the starting concentration was about 1 μg/L, for some it was higher (see Appendix II). Experiments were carried out both at pH 8 and pH 6. The pH was adjusted using 0.1 M aqueous HCl solution.

Solutions 1-6 were also used for experiments with MS2 phages. For these experiments a dispersion containing the MS2 phages was added to a beaker, and mixed for 10 s at 400 rpm. After addition of HCl, in order to adjust the pH, the mixture again was stirred for 10 s at 400 rpm. Subsequently, ferrate solution was dosed and mixed for 15 s at 400 rpm. Flocculation took place during 15 min. at 70 rpm, and then the mixture was allowed one hour for precipitation. A sample was taken from the supernatant and filtered over 0.45 μm filter. The temperature used was 17-18 °C.

3.3 Experiments with dry ferrate

As the ferrate seemed to react immediately with the buffer solution, some extra experiments were carried out using dry ferrate that was directly dissolved in 1.8 L of the solution to which the pharmaceuticals were added. pH was not adjusted, but appeared to be > 8. The composition of the solutions thus obtained in shown in Table 3-4.

Table 3-4: Composition of solutions made without a buffer, directly dissolving dry ferrate

Solution	Sample	Dry ferrate (mg)	Ferrate conc. (mg/L)	pH
7	Commercial Fe(V)	67	1.34	8.80
8	Fe(IV)	25	1.17	8.62
9	Fe(V)	23	1.70	8.94

4 Results and discussion

4.1 Experiments with dissolved ferrate

According to prof. Sharma ferrate solutions at pH 9 should be stable, at least for some days; two weeks were mentioned. However, as already mentioned in section 3.2, it seemed that directly after preparation of the stock solution some reaction occurred. The changing color and gas evaporation seem to indicate that the ferrate reacted with water or possibly NOM, resulting in reduced iron species en possibly oxygen. This may have decreased the reactivity of the ferrate towards both disinfection and oxidation reactions. Their reactivity, however, still was tested after 2-3 days, as described in the following sections.

4.1.1 Disinfection capacity in dissolved ferrate

An MS2 solution theoretically containing$5.0*10^3$ pve/ml was used. The concentration in the influent was determined at four moments, before the start of the experiment. Subsequently two blank experiments, without ferrate were carried out, and experiments were carried out using solutions 1, 2 and 3 (in duplo). The results are shown in Table 4-1.

Table 4-1: results of disinfection experiment

Sample	Pve/ml
Influent t=0	$5.4*10^3$
Influent t = 1	$3.9*10^3$
Influent t = 3	$4.9*10^3$
Influent t = 4	$3.9*10^3$
Blank 1	$4.0*10^3$
Blank 2	$3.4*10^3$
Solution 1a	$5.3*10^3$
Solution 1b	$5.7*10^3$
Solution 2a	$4.9*10^3$
Solution 2b	$5.8*10^3$
Solution 3a	$7.0*10^3$
Solution 3b	$5.9*10^3$

Based on the results shown in Table 4-1 it can be concluded that the solutions used in this experiment were not effective in causing deactivation of the MS2 phages. However, this may be due to the reduced reactivity in the samples, resulting from the reactions of the ferrate upon dissolution. Besides, ferrate concentrations in the samples were relatively low compared to what is often used in literature (1 mg/L instead of 5 mg/L, although [Jiang, 2013] mentions 1.5 mg/L).

4.1.2 Oxidation reactions in dissolved ferrate

The results obtained with dissolved ferrate samples (solutions 1-6) and a mixture of spiked pharmaceuticals are shown in Figure 4-1, Figure 4-2 and Figure 4-3.

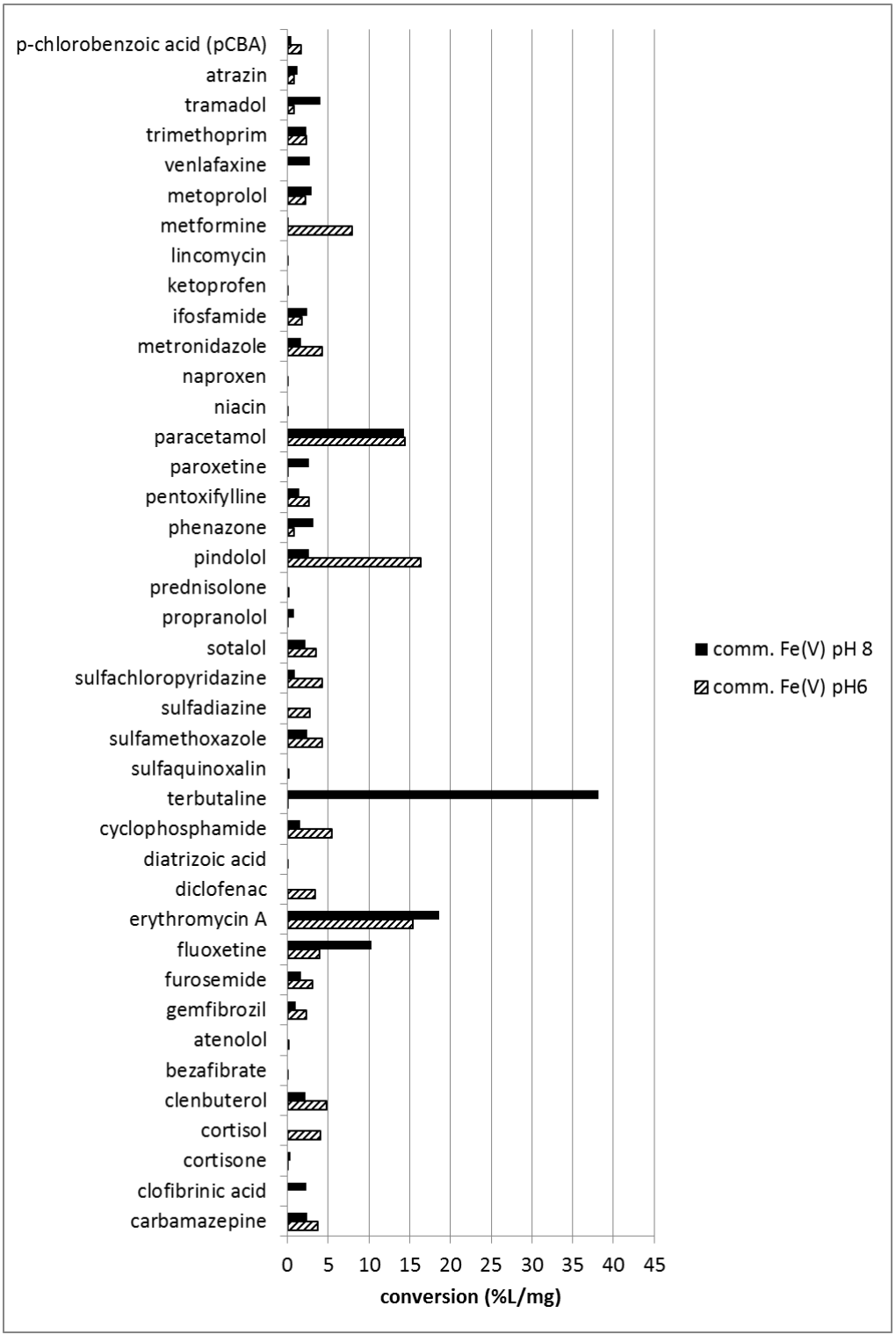

Figure 4-1: Comparison of effectiveness of dissolved commercial Fe(V) at pH 6 and 8 (solutions 1 and 2)

In Figure 4-1the conversion is calculated as a function of the (theoretical) ferrate concentration in the solution. Probably the actual concentration was lower, as the ferrate seemed to react with the water upon dissolution. The conversion is low (< 20%L/mg), except

for terbulaline at pH 8. It can be concluded that there is no significant difference between the overall activity of the ferrate (V) at pH6 or pH8. Differences that can be observed may be attributed to the individual compounds and their behavior at different pH values, which is in accordance with literature [Jiang et al., 2013]. For paracetamol and erythromycin A a conversion of about 15% was obtained, and there seems to be no real difference in behavior at pH 6 or 8. Fluoxetine (pKa = 9.8) and terbutaline (pKa = 8.9) seem to show a higher conversion at pH 8 than at pH 6. However, pindolol (pKa = 0.2) and metformin (pKa = 12.3) seem to more efficiently converted at pH 6 than at pH8. Obviously, this cannot be explained form a difference in pKa value. However, with the low conversions obtained in this case, it is questionable whether the differences observed are significant. The low conversion probably is caused by the low ferrate concentrations used (1.2 mg/L compare to 5mg/L as reported in literature), and the fact that the ferrate concentrations may have decreased by direct the reaction upon dissolution.

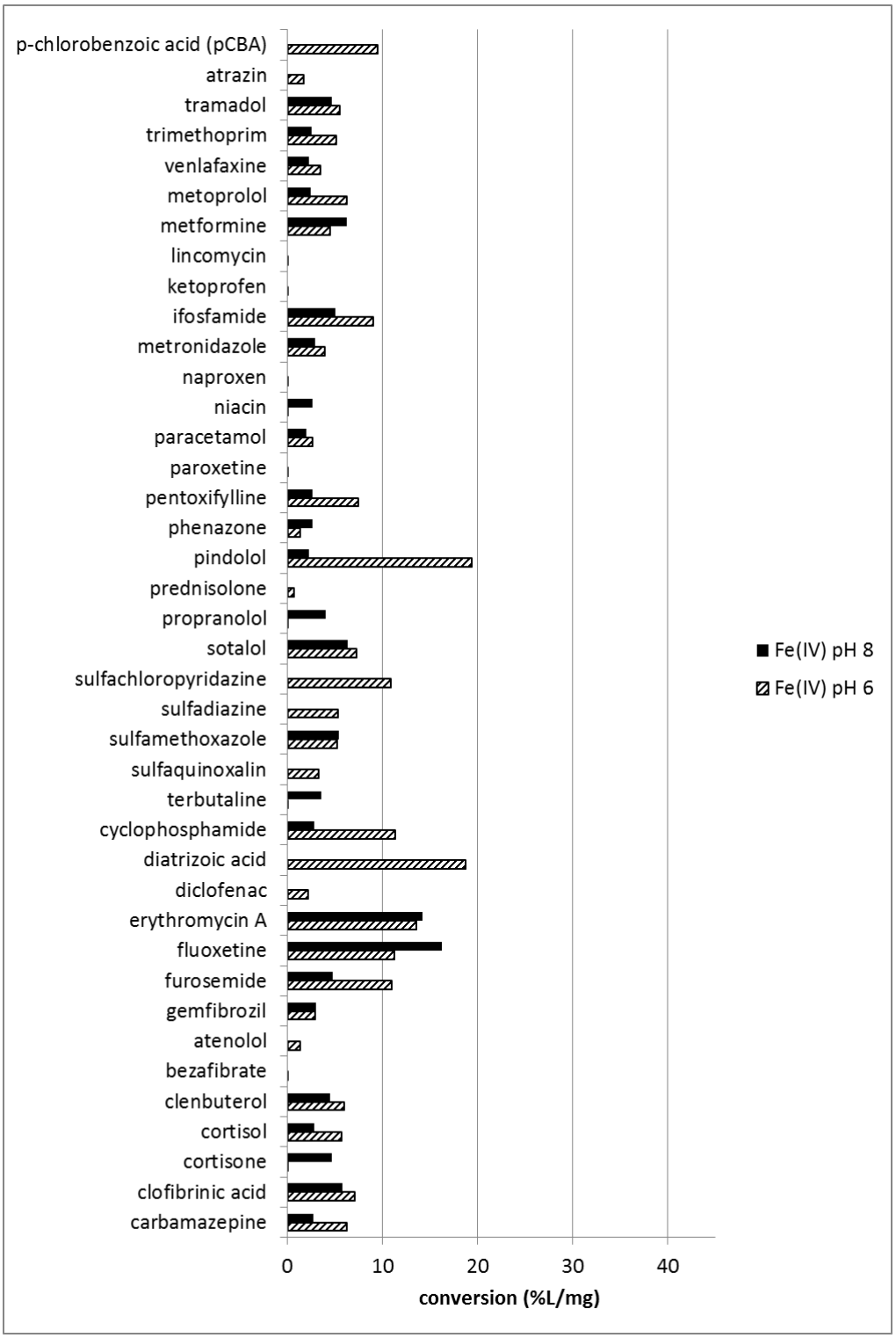

Figure 4-2: comparison of effectiveness of dissolved Fe(IV) at pH 6 and 8 (solutions 3 and 4)

For solutions with Fe(IV) it seems that at pH 6 higher conversions can be obtained than at pH 8, although again it has to be kept in mind that the overall conversion is quite low (< 20% L/mg), due to a low ferrate concentration and reactions upon dissolving the ferrate in the buffer solution. For fluoxetine a higher conversion seems to be obtained at pH 8 and for pindolol at pH 6, which is in accordance with the results obtained with commercial Fe(V).

The results obtained with Fe(V) are shown in Figure 4-3:

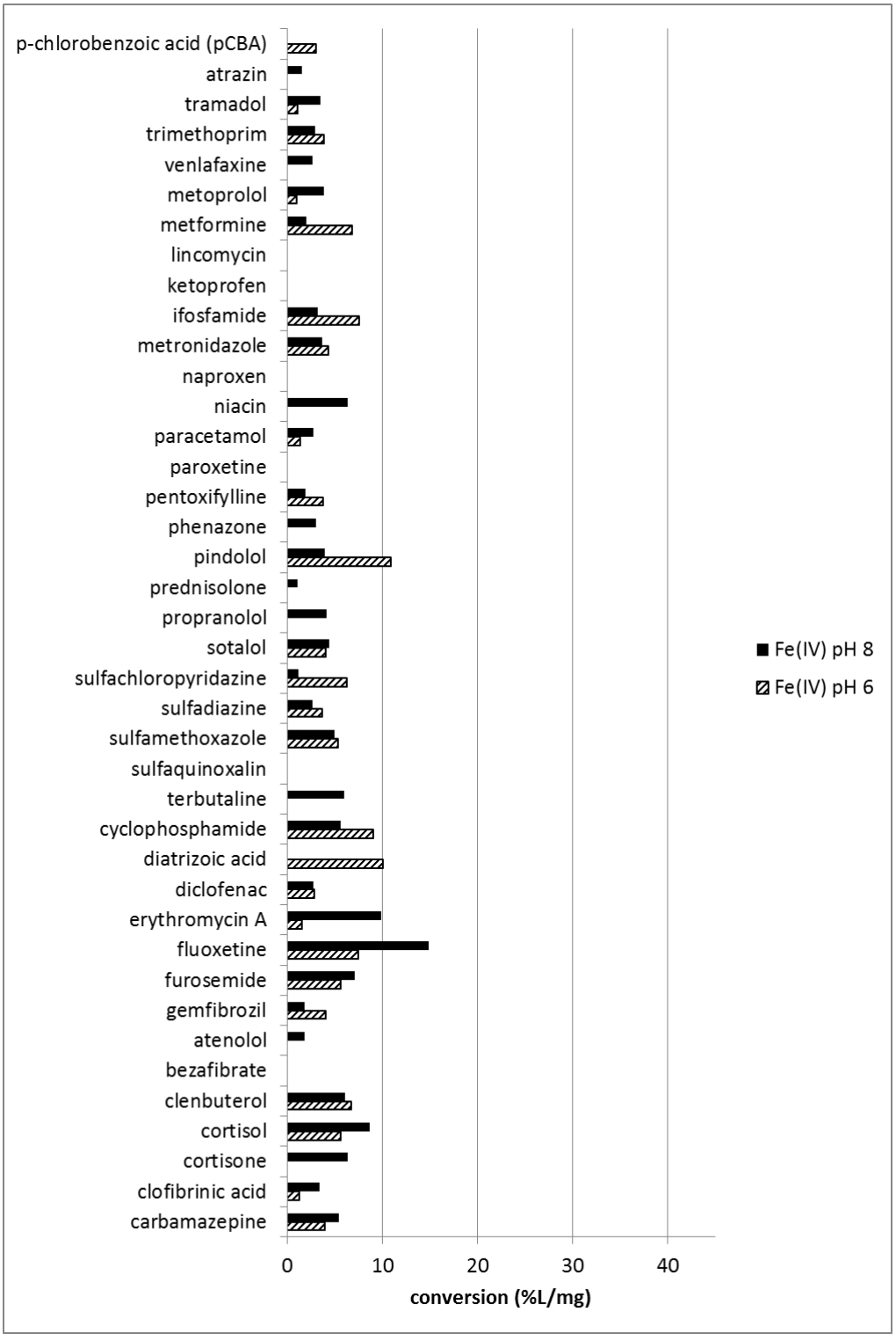

Figure 4-3: comparison of effectiveness of dissolved Fe(V) at pH 6 and 8 (solutions 5 and 6)

In accordance with the results obtained for commercial Fe(V) here too no significant difference between the overall activity of the ferrate (V) at pH6 or pH8 can be observed, although again the overall conversion was low (<15%L/mg). Again fluoxetine seems to be more efficiently converted at pH 8. When comparing the results obtained with Fe(IV) and Fe(V) it can be seen that in general the same results can be found: ifosfamide, pindolol, sulfachloropyridazine, cyclophosphamide, diatrizoic acid and pentoxyfylline are more efficiently oxidized at pH 6 than at pH 8 which is in accordance with literature data, stating that ferrate is a more efficient oxidant at lower pH values.

4.2 Experiments with solid ferrate

For these experiments solid ferrate was added to the aqueous solution containing organic micropollutants. The results are shown in Figure 4-4 and Figure 4-5. Although the concentration of ferrate was relatively low (1.7 mg/L, while normally 5 mg/L is used), a rather good conversion could be obtained. For comparison the conversion was also calculated per mg ferrate (Figure 4-5). From this figure it seems that Fe(IV) is more effective than Fe(V), which is a rather surprising result. In literature in most cases Fe(V) is found to be the more active oxidant. Besides, it can be observed that the commercial Fe(V) is more active than the other Fe(V), but less than the Fe(IV). Maybe Fe(IV) is more stable, and thus easier to handle and to keep. However, in general it can be concluded that ferrate can be a very effective compound to convert organic micropollutants, especially as it also seems to be rather effective in converting compounds like metformin, which are difficult to degrade using other (advanced) oxidation techniques like UV/H_2O_2.

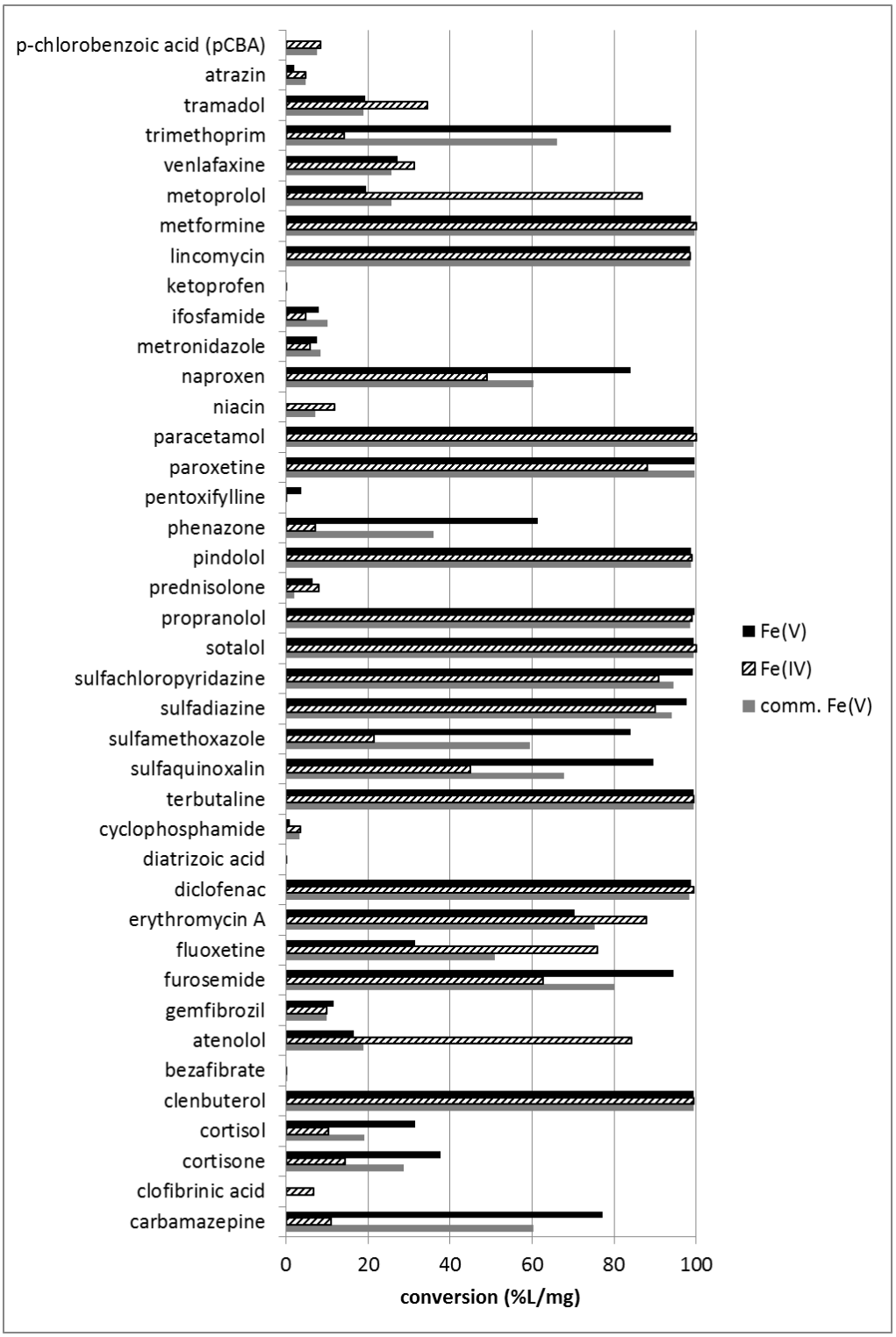

Figure 4-4: Total conversion obtained with 1.7 mg dry ferrate per L, added to solution at pH ≈8.

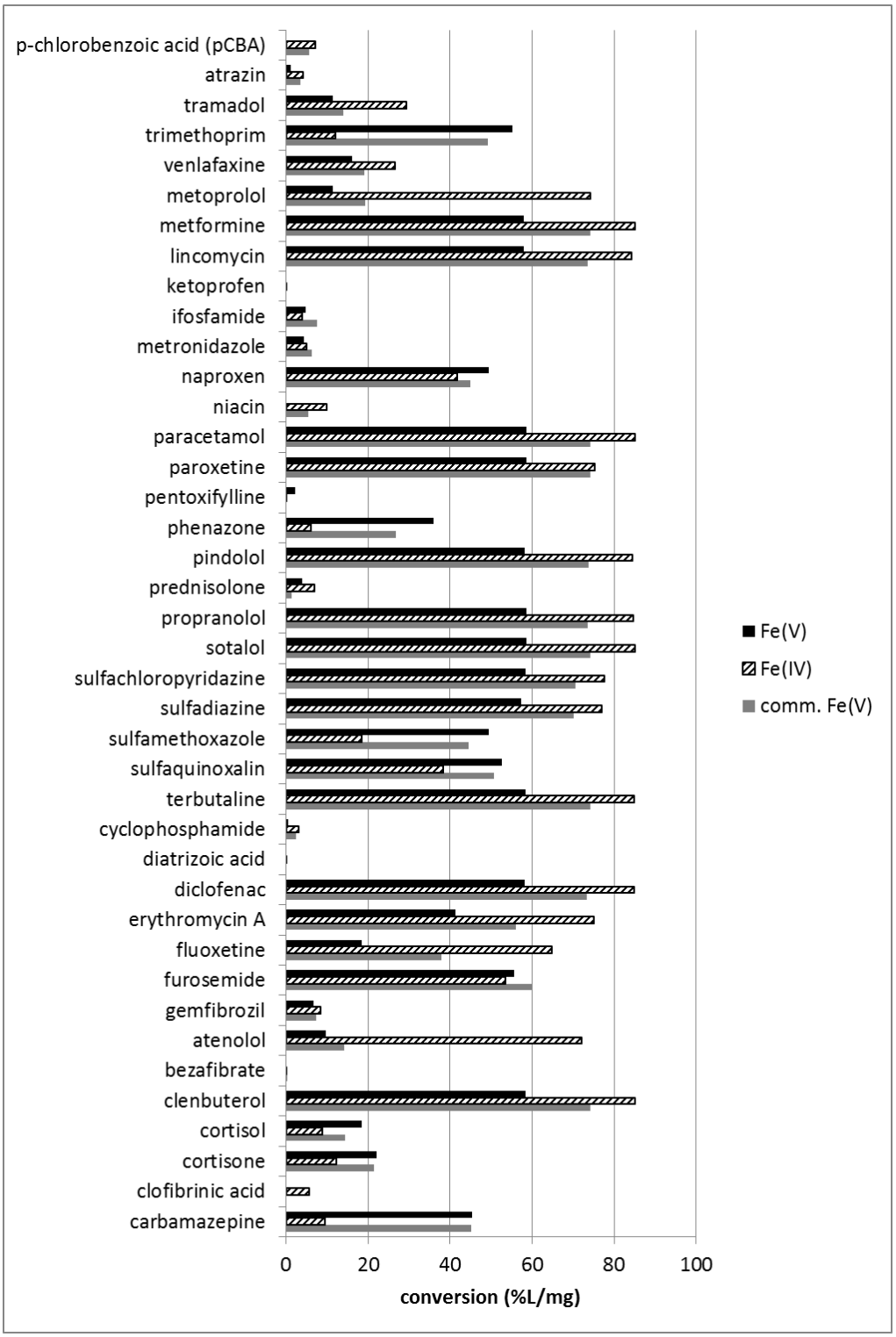

Figure 4-5: Oxidation by solid ferrate (as %L/mg), added to solution at pH ≈8

4.3 Ferrate in water treatment

In principle addition of ferrate gives the possibility to combine oxidation and flocculation in one step. Addition of ferrate (IV, V or VI) instead of Fe(III) as one of the first process steps in

surface water treatment, however, probably will not be very efficient for oxidation of organic micropollutants. Although ferrate is a very effective oxidant, large amounts would be required in order to oxidize both natural organic matter and organic micropollutants, which are present in much lower concentrations. However, as a subsequent treatment step it can be a very interesting possibility. Another interesting application in water treatment is oxidation of metals like iron, manganese and arsenic (Ghernaout and Naceur, 2011; Jain et al., 2009; Sharma 2010, Sharma 2011). Combining oxidation and flocculation in such applications can be a very interesting option.

For large scale applications dosing of ferrate solutions is preferable to dosing dry ferrate. Handling of the material, mixing with the water that should be treated and obtaining desired concentrations is easier with solutions than with dry material. However, the present experiments seem to indicate that it still may be “difficult” to keep ferrate solutions stable for a while. This problem will have to be solved before ferrate really can be applied on large scale. However, the present results indicate that ferrate in itself may be a very interesting compound for use in water treatment, as it is known as a “green” chemical, and can be used to obtain oxidation, disinfection and coagulation in one step, at relatively low energy costs. Therefore, further research into possible applications of ferrate and to find solutions to the stability problem certainly will be worthwhile.

At the moment it is difficult to give an indication of the costs involved in the use of ferrate. Sigma Aldrich sells K_2FeO_4 for about €2000 per 500 g. We obtained the materials tested from a laboratory, so at the moment it is not possible to indicate what the commercial costs of these materials would be.

5 Conclusions and recommendations

5.1 Conclusions

- Dissolving ferrate in a buffer solution resulted in an immediate reaction, as a result of which the concentrate of active ferrate probably was much lower than planned. Although in literature it is suggested that ferrate solutions at pH 9 can be kept stable for several days, these results seem to indicate that this not always is the case.
- Adding dry ferrate to a solution of organic micropollutants results in a very efficient conversion of the micropollutants. For some compounds, like metformin and terbutalin, which are difficult to convert using e.g. UV/H_2O_2 processes, addition of ferrate may be a very effective alternative.
- Contrarily to what is shown in literature, Fe(IV) seems to be more a more effective oxidant than Fe(V). This may be caused by the higher reactivity of Fe(V), making it more difficult to keep it stable in the Fe(V) form.
- Ferrate can be a very efficient means to degrade organic micropollutants, and subsequently cause coagulation (in this case the latter was not tested, as the Nieuwegein tapwater, used for these tests, contains not enough NOM). According to literature, ferrate may also be used for the removal of metals like manganese or arsenic. It certainly seems worthwhile to further investigate the possibilities.

5.2 Recommendations

- Further experiments should be carried out using higher Ferrate concentrations, at about 5 mg/L. Disinfection experiments should be repeated at this higher concentration.
- It may be better to use solid ferrate, but this could be a problem for application at a large scale (dosage and mixing of a solution is easier than of a solid). A way has to be found how to prevent the ferrate from reacting directly upon dissolution. Maybe another solution pH can be applied (>9).
- In this project coagulation by the Fe(III) formed was not tested. The reason was that in Nieuwegein tapwater there is not enough NOM present for coagulation experiments, and from previous research it already is known that Fe(III) is an effective coagulant. However, in a subsequent project coagulation by Fe(III) formed during oxidation should be involved.
- At the moment, with still some experimental ferrate samples or small scale commercial ferrate samples available for testing, it is very difficult to make a realistic cost estimation. However, research into the production and stability of ferrate is being carried out, and in future it may become available at a large scale and at acceptable costs.
- There are several reasons why continuing ferrate research would be worthwhile: (1) ferrate is considered to be a “green” chemical, (2) it may combine several processes (oxidation, disinfection and coagulation), and (3) use of ferrate in water treatment will involve low energy costs.

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Appendix I

Analysis of ferrate samples used

Mössbauer spectrometry analysis:

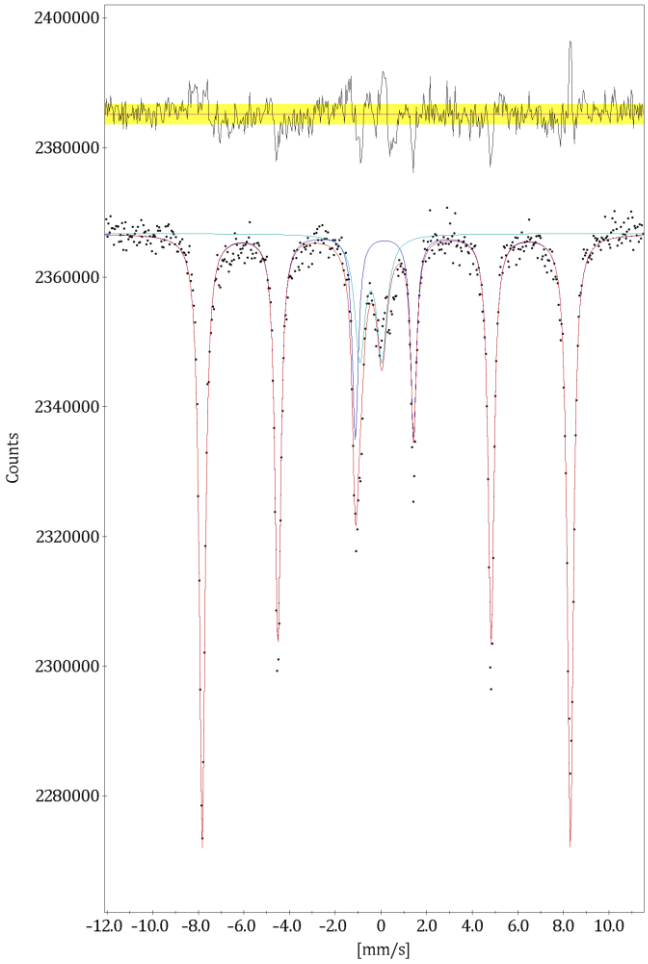
Mössbauer spectrometry is based on a recoil-free absorption and emission of γ-fotons by ^{57}Fe atomic nuclei. The method gives selective information about iron atoms – oxidation state, symmetry of iron close neighborhood, magnetic properties and distribution of iron atoms in nonequivalent phases. The method is used for identification of iron bearing phases and quantification of relative atomic ratios in those phases.

Atomic Absorption Spectrometry analysis:

Atomic absorption spectrometry with flame ionization is used for determination of iron in samples.

Commercial ferrate (LAC company)

Mössbauer spectrometry analysis:



Parameter	Value	StD
(0) Base Line:	2366663.82711	94.98056
$KFeO_2$:	**[85.365 %]**	[Mixed M+Q]
(1) AMPLITUDE:	15329.64071	107.20903
(1) ISOMER SHIFT:	0.19004	0.00090
(1) MAGNETIC FIELD [T]:	50.14016	0.00655
(1) Q. SPLITTING:	0.07856	0.00180
(1) LINE WIDTH:	0.30942	0.00272
K_3FeO_4:	**[14.635 %]**	[Quadrupole]
(2) AMPLITUDE:	15768.81201	414.11900
(2) ISOMER SHIFT:	-0.44522	0.01036
(2) Q. SPLITTING:	0.96770	0.01901
(2) LINE WIDTH:	0.53636	0.02316

Sample contains 85.365% iron atoms in $KFeO_2$ phase and 14.635% iron atoms in K_3FeO_4 phase.

Atomic Absorption Spectrometry analysis:

Sample contains 24.52 weight % of iron.

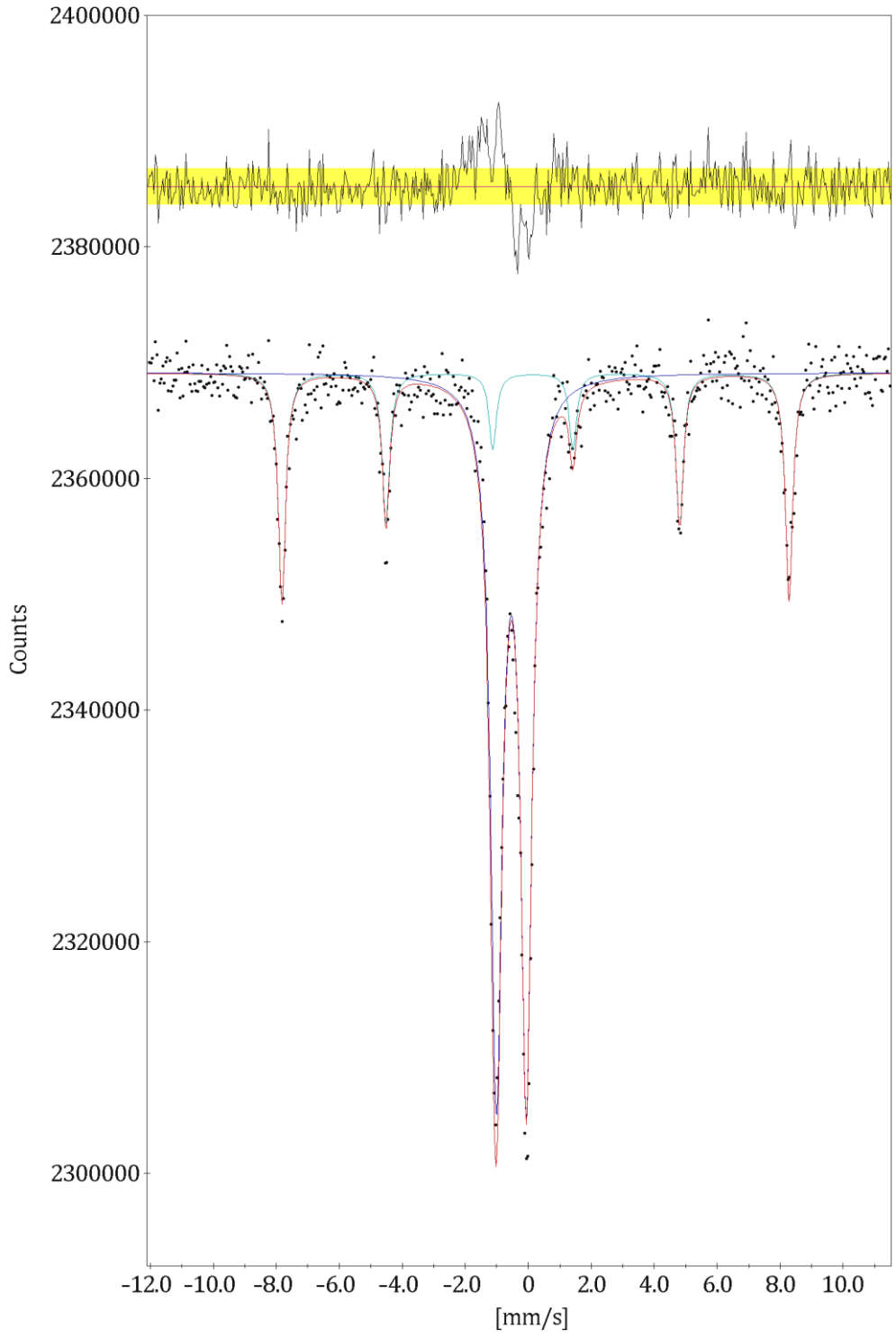
Results:

Sample	Commercial ferrate (LAC company)	
	Relative area of subspectra [%]	Weight of phase [%]
K_3FeO_4	14.635	15.238
$KFeO_2$	85.365	47.580
Non-iron phase		37.182
Sum:	**100.000**	**100.000**

Sample contains 15.238 weight % of ferrate (V), 47.580 weight % of $KFeO_2$ phase and 37.812 weight % of non-iron phases. Non-iron phases present mainly potassium oxides, peroxides, superoxides, hydroxides and possibly nitrates with nitrites (KOH, K_2O, KO_2, K_2O_2, KNO_3 + KNO_2).

K_3FeO_4 (ferrate V)

Mössbauer spectrometry analysis:



Parameter	Value	StD

(0) Base Line:	2369097.03886	90.83539
K_3FeO_4:	**[70.338 %]**	[Quadrupole]
(1) AMPLITUDE:	41647.73944	338.18457
(1) ISOMER SHIFT:	-0.54496	0.00208
(1) Q. SPLITTING:	0.95048	0.00390
(1) LINE WIDTH:	0.42986	0.00523
$KFeO_2$:	**[29.662 %]**	[Mixed M+Q]
(2) AMPLITUDE:	2927.23297	103.06932
(2) ISOMER SHIFT:	0.17961	0.00405
(2) MAGNETIC FIELD [T]:	50.05856	0.03023
(2) Q. SPLITTING:	0.08354	0.00807
(2) LINE WIDTH:	0.28146	0.01291

Sample contains 29.662% iron atoms in $KFeO_2$ phase and 70.338% iron atoms in K_3FeO_4 phase.

Atomic Absorption Spectrometry analysis:

Sample contains 18.89 weight % of iron.

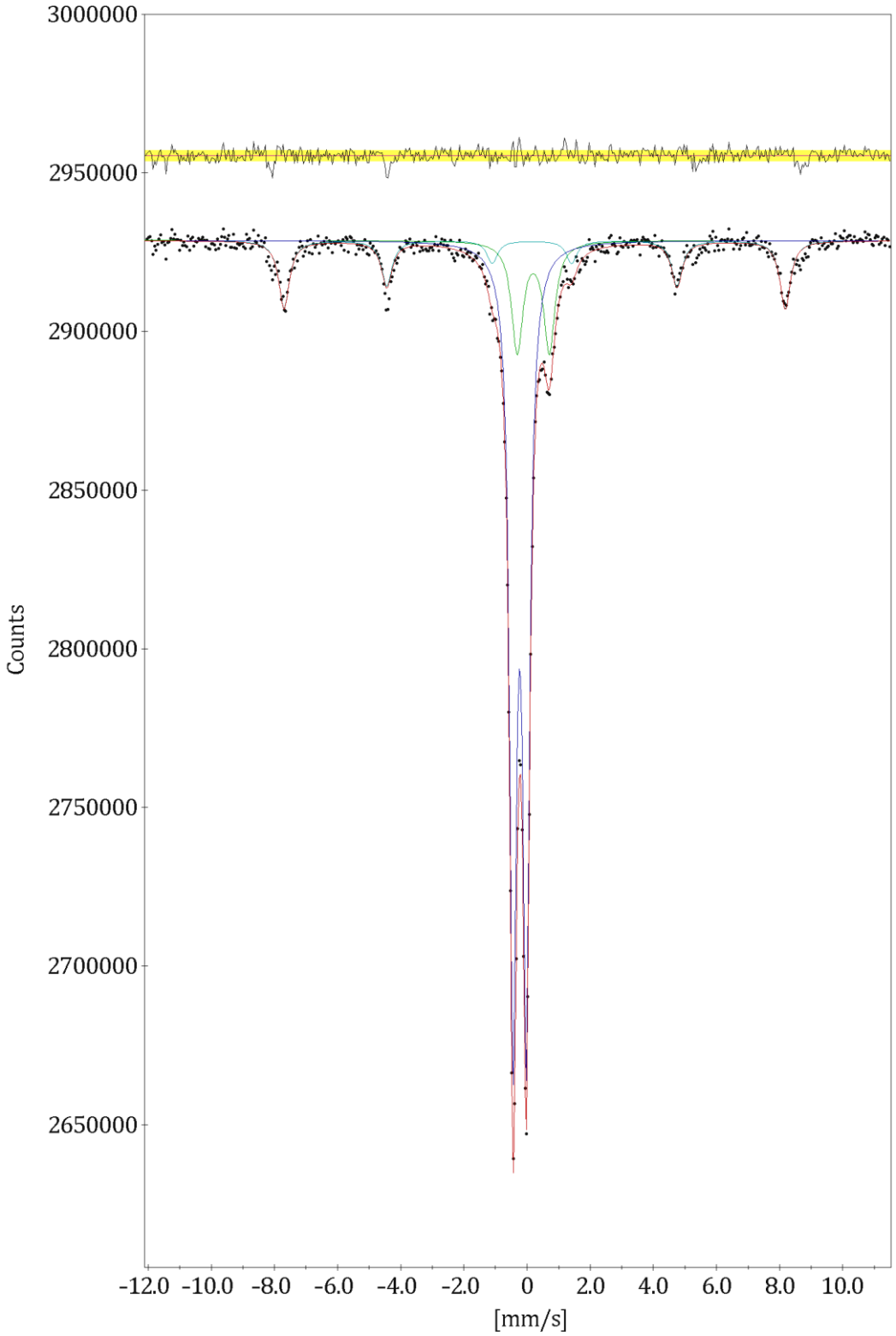
Results:

Sample	K_3FeO_4	
	Relative area of subspectra [%]	Weight of phase [%]
K_3FeO_4	70.338	73.236
$KFeO_2$	29.662	16.533
Non-iron phase		10.231
Sum:	**100.000**	**100,000**

Sample contains 73.236 weight % of ferrate (V), 16.533 weight % of $KFeO_2$ phase and 10.231 weight % of non-iron phase. Non-iron phase formed mainly potassium oxides, peroxides, superoxides, hydroxides and possibly nitrates with nitrites (KOH, K_2O, KO_2, K_2O_2, KNO_3 + KNO_2).

Na_4FeO_4 (ferrate IV)

Mössbauer spectrometry analysis:



Parameter	Value	StD
(0) Base Line:	2928537.30874	115.07368
Na_4FeO_4:	**[65.959 %]**	[Quadrupole]
(1) AMPLITUDE:	98201.04137	429.08330
(1) ISOMER SHIFT:	-0.24029	0.00046
(1) Q. SPLITTING:	0.41581	0.00098
(1) LINE WIDTH:	0.25510	0.00133
$NaFeO_2$:	**[18.334 %]**	[Mixed M+Q]
(2) AMPLITUDE:	4549.39923	157.37083
(2) ISOMER SHIFT:	0.19141	0.00324
(2) MAGNETIC FIELD [T]:	49.33591	0.03630
(2) Q. SPLITTING:	0.08623	0.00959
(2) LINE WIDTH:	0.40304	0.01772
SP $NaFeO_2$:	**[15.707 %]**	[Quadrupole]
(3) AMPLITUDE:	23384.09160	604.49003
(3) ISOMER SHIFT:	0.19141	0.00324
(3) Q. SPLITTING:	1.01539	0.00818
(3) LINE WIDTH:	0.42834	0.01297

Sample contains 34.041% iron atoms in $KFeO_2$ phase (paramagnetic and superparamagnetic phase) and 65.959% iron atoms in Na_4FeO_4 phase.

Atomic Absorption Spectrometry analysis:

Sample contains 12.81 weight % of iron.

Results:

Sample	Na_4FeO_4	
	Relative area of subspectra [%]	Weight of phase [%]
Na_4FeO_4	65.959	32.046
$NaFeO_2$	34.041	8.654
Non-iron phase		59.300
Sum:	**100.000**	**100.000**

Sample contains 32.046 weight % of ferrate (IV), 8.654 weight % of $NaFeO_2$ phase and 59.300 weight % of non-iron phase. Non-iron phase formed mainly sodium oxides, peroxides and hydroxides (NaOH, Na_2O, Na_2O_2).

Appendix II

Oxidation with dissolved ferrate and with solid ferrate

Table II-: composition of solutions 1-6 (µg/L)

compound	blank	Sol. 1	Sol.2	Sol.3	Sol.4	Sol.5	Sol.6
Carbamazepine	1,03	0,984	1	0,984	1,01	0,992	0,978
Clofibrinic acid	1,01	1,01	0,982	0,959	0,968	0,998	0,978
Cortisone	2,36	2,37	2,35	2,4	2,28	2,39	2,22
Cortisol	2,45	2,33	2,47	2,35	2,4	2,32	2,25
Clenbuterol	0,891	0,84	0,867	0,853	0,862	0,835	0,84
Bezafibrate	0,707	0,723	0,742	0,729	0,752	0,735	0,729
Atenolol	0,997	0,995	0,998	0,988	0,997	0,999	0,98
Gemfibrozil	0,786	0,764	0,776	0,77	0,769	0,756	0,773
Furosemide	1,02	0,983	1	0,94	0,985	0,966	0,952
Fluoxetine	1,07	1,02	0,938	0,984	0,945	0,995	0,921
Erythromycin A	0,206	0,168	0,16	0,186	0,185	0,203	0,187
Diclofenac	0,79	0,758	0,798	0,778	0,793	0,769	0,77
Diatrizoic acid	0,833	0,847	0,999	0,721	0,878	0,754	0,864
Cyclophosphamide	0,686	0,641	0,673	0,63	0,672	0,628	0,65
Terbutaline	0,751	1,01	0,407	1,03	0,732	1,06	0,709
Sulfaquinoxalin	0,846	0,845	0,869	0,826	0,872	0,85	0,867
Sulfamethozazole	0,998	0,947	0,969	0,961	0,959	0,948	0,952
Sulfadiazine	0,922	0,892	0,968	0,887	0,928	0,89	0,899
Sulfachloropyridazine	0,731	0,694	0,723	0,674	0,735	0,688	0,723
Sotalol	0,96	0,92	0,935	0,91	0,916	0,924	0,92
Propranolol	1,04	1,1	1,03	1,09	1,01	1,11	1
Prednisolone	4,11	4,1	4,12	4,09	4,19	4,18	4,07
Pindolol	0,438	0,352	0,424	0,377	0,431	0,393	0,422
Fenazone	1,05	1,04	1,01	1,04	1,03	1,05	1,02
Pentoxifylline	0,9	0,872	0,884	0,852	0,883	0,868	0,884
Paroxetine	5,38	6,53	5,21	6,6	5,74	6,9	5,59
Paracetamol	1	0,827	0,828	0,981	0,986	0,987	0,974
Niacin	0,891	1,22	1,01	1,13	0,874	1,14	0,838
Naproxen	0,888	0,939	1,02	0,922	0,895	0,92	0,971
Metronidazole	0,968	0,918	0,949	0,941	0,948	0,929	0,935
Ifosfamide	0,801	0,784	0,778	0,749	0,772	0,744	0,777
Ketoprofen	0,726	0,782	0,799	0,781	0,793	0,776	0,782
Lincomycin	0,357	0,77	0,624	0,897	0,648	0,968	0,719
Metformin	5,97	5,4	5,96	5,78	5,7	5,59	5,86
Metoprolol	1,12	1,09	1,08	1,07	1,1	1,11	1,08
Venlafaxine	1,21	1,21	1,17	1,18	1,19	1,23	1,18

Trimethoprim	1,1	1,07	1,07	1,06	1,08	1,06	1,07
Tramadol	1,02	1,01	0,97	0,98	0,986	1,01	0,987
Atrazine	1	0,991	0,985	0,988	1,01	1,01	0,986
p-chlorobenzoic acid (pCBA)	8,35	8,18	8,3	7,78	8,51	8,11	8,48

Table II-: composition of solutions 7-9 (µg/L)

compound	blank	Sol. 7	Sol.8	Sol.9
Carbamazepine	1,03	0,408	0,917	0,235
Clofibrinic acid	1,01	1,08	0,943	1,04
Cortisone	2,36	1,68	2,02	1,47
Cortisol	2,45	1,98	2,2	1,68
Clenbuterol	0,891	0,005	0,005	0,005
Bezafibrate	0,707	0,706	0,715	0,748
Atenolol	0,997	0,808	0,157	0,832
Gemfibrozil	0,786	0,708	0,709	0,695
Furosemide	1,02	0,201	0,381	0,056
Fluoxetine	1,07	0,526	0,258	0,733
Erythromycin A	0,206	0,051	0,025	0,061
Diclofenac	0,79	0,013	0,005	0,009
Diatrizoic acid	0,833	1,05	0,92	0,943
Cyclophosphamide	0,686	0,664	0,662	0,68
Terbutaline	0,751	0,005	0,005	0,005
Sulfaquinoxalin	0,846	0,272	0,467	0,088
Sulfamethozazole	0,998	0,404	0,784	0,159
Sulfadiazine	0,922	0,054	0,092	0,022
Sulfachloropyridazine	0,731	0,04	0,067	0,006
Sotalol	0,96	0,005	0,005	0,005
Propranolol	1,04	0,014	0,01	0,004
Prednisolone	4,11	4,03	3,78	3,84
Pindolol	0,438	0,005	0,005	0,005
Fenazone	1,05	0,673	0,975	0,406
Pentoxifylline	0,9	0,918	0,94	0,866
Paroxetine	5,38	0,025	0,639	0,025
Paracetamol	1	0,005	0,005	0,005
Niacin	0,891	0,827	0,787	1,01
Naproxen	0,888	0,352	0,454	0,141
Metronidazole	0,968	0,886	0,911	0,895
Ifosfamide	0,801	0,72	0,764	0,737
Ketoprofen	0,726	0,756	0,765	0,773
Lincomycin	0,357	0,005	0,005	0,005
Metformin	5,97	0,025	0,025	0,075
Metoprolol	1,12	0,831	0,148	0,902
Venlafaxine	1,21	0,899	0,833	0,88
Trimethoprim	1,1	0,373	0,945	0,068
Tramadol	1,02	0,828	0,67	0,824
Atrazine	1	0,953	0,952	0,98
p-chlorobenzoic acid (pCBA)	8,35	7,71	7,65	8,76