TECHNICAL UNIVERSITY OF LIBEREC
Faculty of Mechatronics, Informatics and Interdisciplinary Studies

UTILIZATION OF IRON IN A HIGH OXIDATION STATE FOR THE TREATMENT OF CONTAMINATED WATER

PhD Thesis

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ANNOTATION

Iron, one of the most abundant elements on earth, offers a unique range of valence states from 0 up to theoretically +8. It commonly exists in the Fe(II) and Fe(III) oxidation states; however, higher oxidation states called ferrates (Fe(IV), (V), (VI)) can be obtained in a strong oxidizing environment. Ferrates possess a range of unique properties, which can be advantageously used in many electrochemical, environmental, and chemical applications, e.g. higher capacity batteries, selective oxidants in organic chemistry, or as a multipurpose water and wastewater treatment chemical. Due to their green nature, which is the centre of attention these days, ferrates have the potential to become one of the chemicals of the future generation.

Ferrate technologies in the field of water and wastewater treatment have also seen increased attention due to their multifunctional properties (oxidant/disinfectant and coagulation/absorption) and environmentally benign character, which can fulfil strict future water standard requirements.

This work is focused on the study of ferrates for the degradation of priority pollutants in water. Priority pollutants are persistent organic pollutants (POPs), which include hexachlorocyclohexanes (HCH), pentachlorophenol (PCP), polychlorinated dibenzodioxines and dibenzofurans (PCDD/F), penta- and hexachlorobenzenes (PeCB, HCB) and polychlorinated biphenyls (PCB). The outcome of this work from the perspective of individual compounds showed that HCH did not react with ferrates; their identified transformation into TCB was caused by the increased pH in the reaction system. Similarly, there is no reactivity of ferrates with PCDD/F, PeCB, HCB and PCB. On the other hand, PCP was found to be totally degraded by ferrates in both a spiked water system as well as in real contaminated groundwater. The effects of the dose and purity of ferrates were studied and discussed. Furthermore, the kinetic constants of PCP degradation in the presence of ferrates were determined in the pH range of 6 to 9. Also, the total mineralization of PCP to chloride anions and carbon dioxide was found and confirmed. During the experiments, ferrates from different suppliers were used and compared. Spectral methods FE SEM with EDS, ICP-OES/MS and spectrophotometry were mostly used for the characterization of the ferrates.

To summarise, this work has shown the limitations of ferrate applicability for the treatment of POPs-contaminated water. A persistence to Fe(VI) attack was confirmed for HCH, PCDD/F, PeCB, HCB and PCB. On the other hand, PCP was very well degraded. Thus, most attention is given to PCP in this paper.

Four scientific papers were written and published on this topic.

ANOTACE

Železo je jedním z nejhojnějších prvků na zemi. Existuje ve valenčních stavech od 0 až po teoretických +8. Nejčastěji se vyskytuje v oxidačním stavu Fe(II) a Fe(III), nicméně vyšší oxidační stavy - ferráty (Fe(IV), (V). (VI)) - lze získat v silném oxidačním prostředí. Ferráty mají řadu unikátních vlastností, které jsou s výhodou využívány v mnoha elektrochemických, environmentálních a chemických aplikacích, jako např. vysokokapacitní baterie, selektivní oxidanty v organické chemii nebo jako víceúčelové činidlo pro úpravu a čištění vod. Díky své „green nature", která je nyní ve středu zájmu, mají ferráty potenciál být jednou z chemikálií budoucích generací.

Velkou pozornosti upoutala technologie ferrátů v oblasti úpravy a čištění vod díky svému multifunkčnímu (oxidant/dezinfektant a koagulant/absorbent) a ekologicky nezávadnému charakteru. Ten může splňovat i přísné budoucí požadavky v oblasti standardu vody.

Tato práce se zaměřuje na studium ferátů pro degradaci prioritních polutantů ve vodě. Prioritními polutanty jsou perzistentní organické látky (tzv. POP), které zahrnují hexachlorocyklohexany (HCH), pentachlorfenol (PCP), polychlorované dibenzodioxiny a dibenzofurany (PCDD/F), penta a hexachlorbenzeny (PeCB, HCB) a polychlorované bifenyly (PCB). Výsledkem práce z pohledu jednotlivých látek POP je, že HCH s ferátem nereagují. Jejich zjištěná transformace na TCB je způsobena pouze zvýšením pH v reakčním systému. Stejně tak feráty nereagují s PCDD/F, PeCB, HCB, ani s PCB. Naopak k totální degradaci ferátem došlo v případě PCP, a to jak v uměle kontaminované tak i v reálně kontaminované podzemní vodě. Studován a diskutován byl vliv dávky a vliv čistoty ferátů. Dále byly stanoveny kinetické konstanty degradace PCP feráty v rozsahu pH od 6 do 9. Také byla potvrzena totální mineralizace PCP na chloridy a oxid uhličitý. Během experimentů byly používány a srovnávány feráty od různých dodavatelů. K charakterizaci ferátů byly používány převážně spektrální metody, jako FE SEM s ECD, ICP-OES/MS a spektrofotometrie.

Tato práce poukazuje na limity využitelnosti ferátů pro čištění vod kontaminovaných POP. Látky HCH, PCDD/F, PeCB, HCB i PCB byly k ferátům persistentní. Naopak PCP bylo velmi dobře degradováno a je mu proto v práci věnována největší pozornost.

Na toto téma byly napsány a otištěny čtyři vědecké publikace.

Klíčová slova: Feráty, Fe(VI), POPs, persistentní organické polutanty, odbouratelnost, pentachlorfenol, hexachlorcyklohexany, PCB, PCDD/F, pentachlorfenol, hexachlorbenzen, oxidace, degradační produkty, reakční kinetika

CONTENTS

ATTACHMENTS

- <u>M. Homolková</u>, P. Hrabák, M. Kolář, M. Černík: Degradability of hexachlorocyclohexanes in water using ferrate (VI). *Water Sci. Technol.* **71**, 405-411 (2015).

- <u>M. Homolková</u>, P. Hrabák, M. Kolář, M. Černík: Degradability of pentachlorophenol using ferrate(VI) in contaminated groundwater. *Environ. Sci. Pollut. Res.* **23**, 1408-1413 (2016)

- <u>M. Homolková</u>, P. Hrabák, N. Graham, M. Černík: A study of the reaction of ferrate with pentachlorophenol − kinetics and degradation products. *Water Sci. Technol.* **75**, 189-195 (2017)

- P. Hrabák, <u>M. Homolková,</u> S. Waclawek, M. Černík: Chemical degradation of PCDD/F in contaminated sediment. *Ecol. Chem. Eng. S.* **23**, 473-482 (2016)

1 ABBREVIATIONS

AAS	atomic absorption spectroscopy
BTEX	benzene, toluene, ethylbenzene, xylenes
CPs	chlorophenols
DBP	disinfection by-products
DDT	dichlorodiphenyltrichloroethane
EDCs	endocrine disrupting chemicals
EDS	Energy-Dispersive X-ray Spectroscopy
ERM	electron-rich organic moiety
FE SEM	Field Emission Scan Electron Microscope
HBQ	halobenzoquinones
HCB	hexachlorobenzene
HCH	hexachlorocyclohexane
HRMS	High-Resolution Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
MTBE	methyl tert-butyl ether
NATO	North Atlantic Treaty Organization
nZVI	nano zero valent iron
PAH	polyaromatic hydrocarbons
PeCB	pentachlorobenzene
PCB	polychlorinated biphenyls
PCDD	polychlorinated dibenzo-p-dioxins
PCDF	polychlorinated dibenzofurans
PCP	pentachlorophenol
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonate
PPCDs	Pharmaceuticals and Personal Care Products
POPs	persistent organic pollutants
SPME	Solid-phase microextraction
TEF	Toxicity Equivalent Factor
THM	trihalomethanes
UPOL	Palacký University Olomouc
USEPA	US Environmental Protection Agency
WWT	Water and Wastewater Treatment

2 INTRODUCTION

Over the last 20 years there has been a boom in the research of ferrates. The number of published ferrate-oriented scientific papers has been growing year on year. According to the literature, these higher oxidation states of iron are generally believed to be applicable in the treatment of any kind of water effluent[1] – for the transformation of inorganic pollutants[2,3], for the degradation of organic pollutants[4–7] including emerging micropollutants[8–14] (EDCs and PPCPs), for water and wastewater disinfection[15–21] (pathogens, bacteria, viruses), for the treatment of sewage sludge[22,23], and for the removal of humic substances[1,24]. Furthermore, Fe(III), the degradation product of ferrate itself, serves as an effective coagulant/flocculant for removing non-degradable impurities[25–29] (heavy metals, radionuclides, turbidity). For these reasons, ferrates can be called an "emerging water-treatment chemical"[8]. To summarize, the enormous potential of ferrate based water-treatment technology is based on the possibility to combine several effects in one dosing unit[13,30–33] – primarily oxidation and precipitation, but also disinfection, and thus the possibility to reduce the costs of the treatment and the required management. Moreover, this technology is a "green"[30] one as it is free from any toxic by-products. Ferrate was first used as a multipurpose water treatment chemical by Murmann and Robinson[34] in 1974.

One of the greatest challenges associated with ferrate is its synthesis. To-date, there is no widely accepted method for reliable and reproducible preparation of high purity ferrate, even though a number of research groups have strived to develop it. Therefore, nowadays, there are many ferrates available on the market which differ significantly in purity. Both the low content of high-valent iron and the significant presence of impurities are relevant problems. Over the past year there has been no commercially available ferrate with a purity of over 90 %.

3 OBJECTIVES

The aim of this work is to determine and verify the degradability of POPs (persistent organic pollutants) by ferrates.

The extraordinary properties of ferrates combined with the high preparation costs of solid ferrates predetermine them as "top oxidants" and as such should be used solely for the treatment of exclusive pollutants. These certainly include POPs, which are the highest priority pollutants in terms of their toxicity, persistence and ubiquitous occurrence.

During the work, the chemical composition of several ferrates available from different suppliers with various purities was characterized and their reactivity and properties were compared.
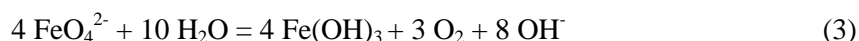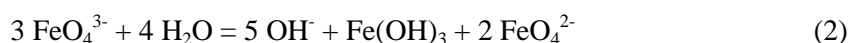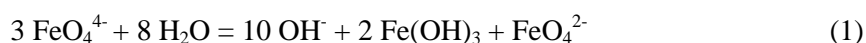
4 THEORETICAL PART

4.1 Ferrates

4.1.1 History

An unstable violet product, later identified as K_2FeO_4, was first discovered by a German physician and chemist Georg Stahl in 1702. In 1834, Mr. Eckenberg and Mr. Bequerel obtained the same colour when heating KOH with iron ore. Mr. Fremy was the first (in the 1840s) to hypothesize that it could be a form of iron with a high oxidation number and the formula could be FeO_3. One hundred years later, the synthesis of ferrates began to be studied systematically[35].

4.1.2 Description

Ferrates are salts of iron in a high oxidation state[30], +4 (FeO_3^{2-}, FeO_4^{4-}), +5 (FeO_4^{3-}), +6 (FeO_4^{2-}), +8 (FeO_5^{2-}). In water, they give a characteristic violet colour similar to that of K-permanganate.

Ferrates are generally quite unstable compounds. Fe(IV) and Fe(V) immediately disproportionate in water[36–38] according to eq. 1 and eq. 2, respectively, to Fe(VI) and Fe(III). Water decomposition (the spontaneous oxidation in water) of Fe(VI) is significantly slower and can be described[31,32] by equation (3).

$$3\ FeO_4^{4-} + 8\ H_2O = 10\ OH^- + 2\ Fe(OH)_3 + FeO_4^{2-} \tag{1}$$

$$3\ FeO_4^{3-} + 4\ H_2O = 5\ OH^- + Fe(OH)_3 + 2\ FeO_4^{2-} \tag{2}$$

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

As this work is devoted to water treatment applications of ferrates, it deals with ferrates dissolved in water. It is therefore appropriate to talk exclusively about Fe(VI), notwithstanding the original oxidation state of iron in the solid powder used for Fe(VI) solution preparation. For this reason, the following text is focused on iron in oxidation state +6 and when not specified otherwise, the general term "ferrate" refers to Fe(VI).

4.1.3 Reactivity and stability

Potassium ferrate is a very powerful and reactive chemical. Its redox potential is +2.20 V or +0.72 V in acidic or alkaline conditions, respectively[39].

Its redox potential under acidic conditions is higher than of any other oxidants/disinfectants used in water and wastewater treatment (WWT), including chlorine, hypochlorite, chlorine dioxide, ozone, hydrogen peroxide, dissolved oxygen or permanganate (Figure 1)[32,40]. However, the order of the redox potentials under alkaline conditions differs significantly and ferrate becomes a relatively mild oxidant.
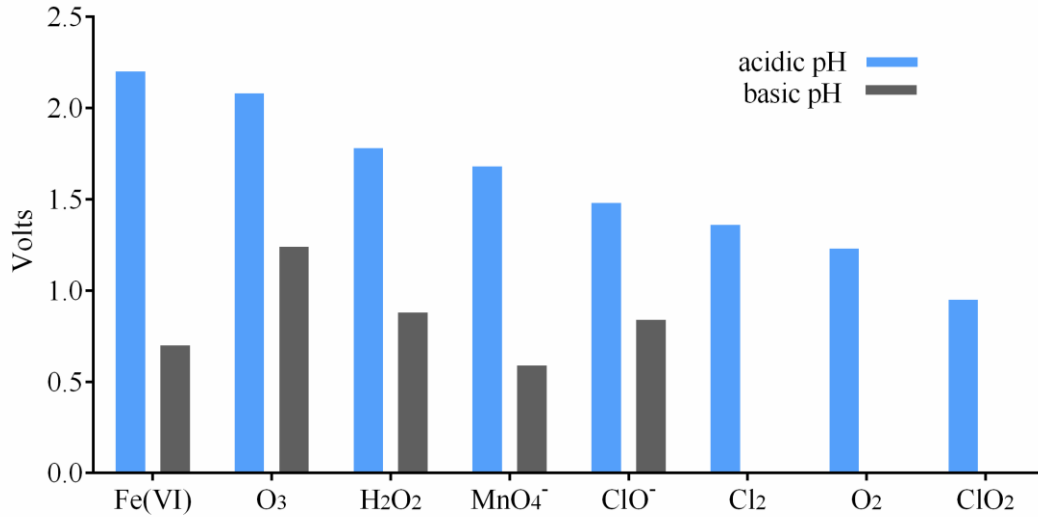

Figure 1: Redox potentials of ferrate and the oxidants/disinfectants used in WWT[32,40]

The difference in the redox potential of Fe(VI) under various pH conditions is caused by its four existing forms, depending on pH: $H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$ and FeO_4^{2-} with pKa 1.6, 3.5 and 7.3, respectively (Figure 2)[41,42,31,43]. FeO_4^{2-} predominates under alkaline conditions and it is the least reactive but the most stable species. The unionized forms of ferrate are stronger oxidants and exhibit an increased reactivity.
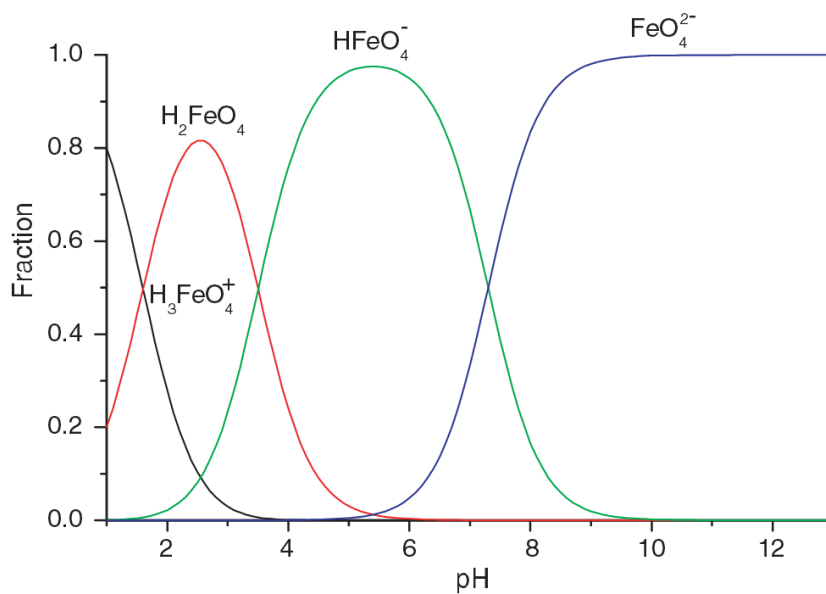

Figure 2: Fe(VI) species under various pH conditions[41,42,31,43]

Ferrate salts are relatively stable in a dry atmosphere; however, they become very unstable when exposed to water and even air humidity[44]. The stability of potassium ferrate in water generally depends on four basic parameters: pH, temperature, ferrate concentration and coexisting ions[32].

As already shown, the stability/reactivity of ferrate and thus its decomposition rate depends significantly on pH. The stability of a solution increases with its alkalinity and/or pH which means that aqueous ferrate is stable under alkaline conditions. The decomposition rate constant has its minimum between pH 9.2 and 9.4. The stability drops rapidly with decreasing pH (Figure 3).
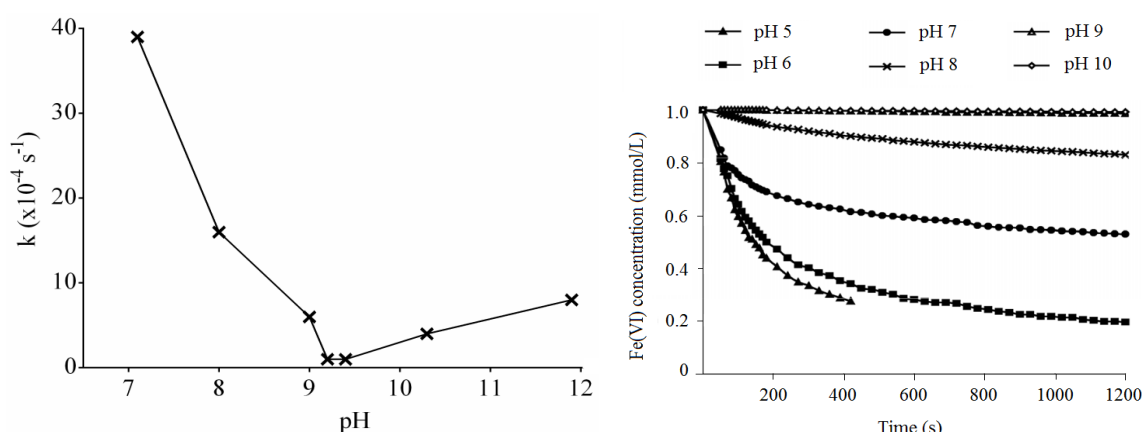

Figure 3: Fe(VI) decomposition rate under different pH conditions (left)[43] and the spontaneous decomposition of Fe(VI) under different pH conditions (right)[30]

Concerning temperature, the reactivity of ferrate with water (eq. 3) follows the Arrhenius law and thus ferrate is stable for a long period of time at lower temperatures. Wagner et al[45] described the reduction of 10 % of 0.01 M Fe(VI) solution after 2 hours at 25 °C, but almost no reduction at 0.5 °C.

The influence of the concentration of the ferrate solution is very significant. Diluted solutions are much more stable than concentrated ones. For example 89 % of initial ferrate will remain in a solution with a concentration of 0.020 and 0.025 M for 1 hour. But almost all of the ferrate is decomposed under the same conditions when the ferrate concentration is over 0.03 M[46]. Autocatalytic decomposition of Fe(VI) to Fe(III) precipitates is probably responsible for this behaviour (eq. 3).

And finally, the presence of coexisting ions, e.g. dissociated NaCl or FeOOH accelerates the rate of ferrate decomposition[46].

The natural occurrence of ferrates is limited to their presence in living organisms, where higher-valent iron complexes play an essential role in the reaction mechanisms of enzymes. Ferryl-oxo

species Fe(IV)=O and Fe(V)=O have been identified as key oxidants in many heme and non-heme enzymes[47–52]. An example is the catalytic cycle of Cytochrome P450 enzymes[53].

4.1.4   Coagulation effect & green chemical

As shown in equation (3), Fe(VI) decomposes in water to Fe(III). This phenomenon results in two very important consequences.

Firstly, Fe(III) is known to be a very powerful coagulant/flocculant[25,26]. So both the oxidation effect of ferrate itself together with the precipitation effect of its product can be used in one step, and thus, more pollutants can be removed from a treated water stream at once.

Secondly, as just the ferric ion is the final product of ferrate decomposition, it is non-toxic, safe, environmentally benign and a micronutrient for plant life[21,31]. For this reason, and omitting the ferrate preparation, ferrate can be called a "green oxidant" as its utilization is, as far as is known, not connected with any of the harmful or often potentially carcinogenic DBPs associated with other disinfectants (chlorine, bromine, iodine, chlorine dioxide, ozone)[2,32,54]. For example, haloforms are connected with the utilization of chlorine[55,56]; ozone can react with a commonly present bromide ion and thus produce a carcinogenic bromate ion[57] (ferrate has no reactivity with bromide[2]); HBQ are connected with chlorination, chloramination, chlorination with chloramination and ozonation with chloramination[58]. The disadvantages and threats (DBPs and their health effects) together with an overview of the operational costs and concerns of commonly used disinfectants/oxidants with an emphasis on chlorine are reviewed in detail by Skaggs[21]. Notwithstanding the fact that ferrates do not produce these DBPs they can even be used for the control of bromate formation. The total reduction of by-products was achieved in a ferrate-ozone-system[59]. The overall effect of oxidative water treatment on toxicity can be accessed by using e.g. the Ames mutagenicity test, which claims to reveal 90 % of all known carcinogens[60]. Ames tests were applied to ferrate-treated water and the preliminary results showed a negative response under the conditions studied[61]. Furthermore, zebra fish embryo tests were performed to compare the toxicity of raw wastewater with ferrate-treated wastewater[62]. The results proved a significantly higher toxicity of the raw water than of the treated effluent. These data suggested that ferrate did not produce mutagenic or toxic by-products. However, other studies reporting potential formation of harmful by-products can also be found (e.g. aldehydes from carbohydrates[63], formaldehyde from methanol[64], p-benzoquinone from phenols[65] or methyl group compounds from sulfamethoxalone[12]). There is clearly still a big need to responsibly study the exact reaction conditions and the original pollutants to establish a definitive conclusion.
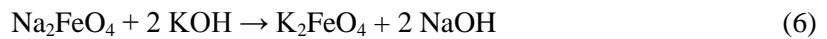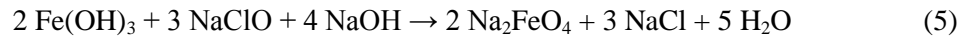
4.1.5 Preparation

There are three ways of preparing potassium ferrate: dry oxidation, wet oxidation and the electro-chemical method[13,30,32].
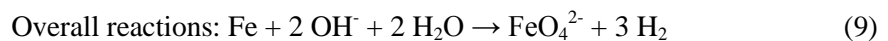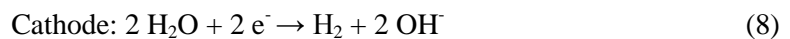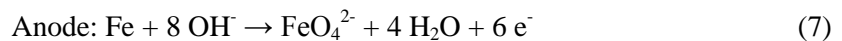
The principle of the oldest method, dry oxidation (or thermal synthesis), lies in the heating/melting of minerals containing iron oxide under strongly alkaline conditions and oxygen flow (eq. 4). This method is considered to be quite dangerous and difficult as it could result in an explosion at elevated temperature. In addition, the yield of this preparation is quite low.

$$Fe_2O_3 + 3\ Na_2O_2 \rightarrow 2\ Na_2FeO_4 + Na_2O \tag{4}$$
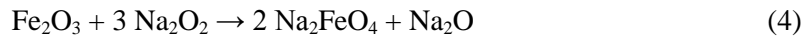
During wet oxidation, Fe(III) salt is oxidized by hypochlorite or chlorine under strongly alkaline conditions (eq. 5). The raw product needs to be precipitated, recrystallized, washed, and dried in order to obtain a solid stable product (eq. 6). The yield of this preparation can be 75 % with a very high purity of the final product of 99 %[43]. This method is considered to be the most practical. On the other hand, a disadvantage leading to strict control of the procedure is the use of hypochlorite resulting in the release of harmful chlorine gas. Furthermore, there is a difficulty with the impurities contained in the material. The alkali metal hydroxides, chlorides and ferric oxide cause rapid ferrate decomposition.

$$2\ Fe(OH)_3 + 3\ NaClO + 4\ NaOH \rightarrow 2\ Na_2FeO_4 + 3\ NaCl + 5\ H_2O \tag{5}$$

$$Na_2FeO_4 + 2\ KOH \rightarrow K_2FeO_4 + 2\ NaOH \tag{6}$$

The electro-chemical method uses anodic oxidation where the iron/alloy is the anode and NaOH/KOH serves as the electrolyte (eq. 7-10). Cast iron dissolves and is oxidised to K_2FeO_4. Factors affecting the yield of this reaction are current density, the composition of the anodes, and the type, concentration, and temperature of the electrolyte. Recently, a novel on-line water purification methodology, *in-situ* electro-chemical preparation of ferrate, has been introduced[66–68]. This could be advantageously used in WWT practice as there is no instability problem and no need of transportation as the ferrate is used directly.

$$\text{Anode: } Fe + 8\ OH^- \rightarrow FeO_4^{2-} + 4\ H_2O + 6\ e^- \tag{7}$$

$$\text{Cathode: } 2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^- \tag{8}$$

$$\text{Overall reactions: } Fe + 2\ OH^- + 2\ H_2O \rightarrow FeO_4^{2-} + 3\ H_2 \tag{9}$$

$$FeO_4^{2-} + 2\ K^+ \rightarrow K_2FeO_4 \tag{10}$$

4.1.6 Ferrate application

As iron is considered non-toxic, potassium ferrate can be advantageously used in many areas and make them environmental friendly[31].

One of the properties of ferrate is that it selectively oxidizes[69] a number of organic compounds, e.g. primary alcohols and amines to aldehydes (not acids), secondary alcohols to ketones, or benzyl alcohol to benzaldehyde (not benzoic acid)[63,70–72]. Therefore, ferrate can be successfully used in environmentally friendly synthesis as a green selective oxidant and thus replace the use of toxic high-valent transition metal oxides.

Another usefulness of ferrate can be seen in the field of higher capacity batteries. The storage capacities of commonly used batteries (zinc and manganese dioxide) are limited mainly by the cathode. Therefore, replacement of MnO_2 with K_2FeO_4[73–75] results in 47 % greater capacity, higher intrinsic energy and better conduction of electricity and recharge ability. Furthermore, the rust from such a "super-iron battery" is much preferable compared to toxic manganese compounds.

Formation of biofilms (bacteria attached to surfaces) is a big problem and complication in many industries. For example, in condenser systems in electric generation plants this can result in a lowering condenser efficiency and electricity generated per unit of fuel. The utilization of Fe(VI) is an environmentally safe but very effective solution to control the biofouling and for keeping the tubes clean[76].

Ferrate can also be used for a novel, fast, safe, highly efficient, ultralow-cost and green synthesis of single-layer graphene oxide[77], which is a precursor of graphene. Thus, the previous procedure involving the utilization of heavy metals and poisonous gases, explosion risk and long reaction times can be replaced.

Finally, the utilization of ferrate which this paper deals with is as a multipurpose water treatment chemical for water disinfection, oxidation, coagulation, and purification[1,31].

4.1.7 Water and wastewater treatment & remediation

There are many different chemicals commonly used in the field of WWT. Among the oxidants/disinfectants applied for the control of pathogens in water and for the removal of chemical pollutants are halogen-based (e.g. chlorine or chlorine dioxide) and oxygen based (e.g. ozone or hydrogen peroxide) chemicals. Coagulation processes are commonly provided by

aluminium or ferric salts. Nevertheless, each oxidant, disinfectant and coagulant has its own limitations (see paragraph 4.1.4).

Commonly used oxidants for remediation of contaminated water include permanganate, persulfate, hydrogen peroxide, Fenton's reagent (H_2O_2 + Fe^{2+}), ozone and peroxon (hydrogen peroxide with ozone). Their reaction rate with pollutants decreases in the following order: Fenton's reagent > ozone > persulfate > permanganate[78]. They are applicable for the elimination of the most common pollutants: petroleum hydrocarbons, BTEX, chlorinated hydrocarbons, MTBE, PAH, herbicides, PCB. Their main limitation is the non-specificity of the chemical oxidation[78], which means that they are applicable to any kind of micropollutant; however, as there are many other non-target pollutants (ballast organic compounds) in real water, oxidants are mostly consumed by the water matrix and thus cannot degrade the desired pollutants sufficiently, and/or their consumption significantly increases. Furthermore, these oxidants are not very effective for remediation of persistent organic pollutants.

Although Fenton's reagent is the most commonly used oxidant, its application is not easy. The stability of this oxidant is of a big concern and is significantly influenced by pH and temperature. Another problem connected with this reagent is the release of high amounts of gases during application.

Ozone is a toxic gas which requires caution during application. Furthermore, due to its high reactivity and instability it has to be produced directly on-site. Another disadvantage is its low solubility in water (6.2 mg/L at 20 °C)[78].

Persulfate is a very powerful oxidant; pollutants tend to mineralize in its presence. Its main limitation is the production of high sulphate concentrations in treated waters, which thereafter cannot be discharged to watercourses. Furthermore, persulfate radical is such a strong oxidant that is can even generate reactive forms of chlorine (including gaseous chlorine) from chlorinated substances[79].

Iron-based technologies are attractive due to their environmentally benign character, as iron is one of the most common elements on earth. It has a number of possible oxidation states which are used for remediation and water treatment (nZVI, part of Fenton's reagent Fe(II), common coagulant Fe(III), emerging oxidant/disinfectant Fe(VI)). Moreover, the general magnetic character of iron materials allows them to be easily removed after application. The promising utilization of ferrate due to its multipurpose character and its green nature has already been mentioned above. Furthermore, the ferrate oxidation process is usually much faster than oxidation carried by permanganate or Fenton's reagent. According to Matějů et al.[78], for example, water needs to remain in a reactor for at least 120 min when using Fenton's reagent. To illustrate the rapidity of ferrate treatment, several kinetic constants of ferrate oxidation are stated

by Sharma[31], Tiwari and Lee[30] or Jiang[13]. One particular example could be that of hydrogen sulphide. Oxygen oxidation of H_2S is a relatively slow process which becomes practical only under pressurized conditions. Oxidation by peroxide is faster but still slow. The reaction of hydrogen sulphide with hypochlorite, chlorine and permanganate is completed within five minutes of contact time, which enables them to be considered as potential oxidizers. However, for a comparison, ferrate oxidation is completed in less than a second[31].

Compared to the non-specific nature of the above-mentioned oxidants, ferrate (and partly ozone) is a selective oxidant targeting compounds containing ERMs (e.g. phenol, olefin, polycyclic aromatics, amine or aniline moieties)[13,80]. Therefore, it is not applicable for the treatment of any kind of micropollutant (e.g. the electron-withdrawing group has less reactivity or a slow reaction rate with ferrate(VI)) but when treating compounds containing ERMs it is much more effective.

The effectiveness of ferrate treatment is also reflected in the dose needed. Very small doses of ferrate are sufficient for pollutant treatment. Lee et al.[8] showed that 1.0 mg/L Fe(VI) is a sufficient dose for 99 % removal of all EDCs studied from both natural water and waste water (pH = 8, t = 25 °C, $[EDCs]_0$ = 0.15 μM, contact time = 30 min). Jiang and Lloyd[32] stated the most efficient molar ratio of ferrate to organic pollutant as being 3-15:1. As common concentrations of pollutants are very low, the required ferrate concentration is also low. This results in another huge advantage, which is a decreased volume of produced sludge[30].

To briefly summarize the advantages of ferrate technology: it is a very powerful, specific, fast, effective, less sludge producing and less material demanding technology.

4.2   Persistent organic pollutants

POPs are organic chemical substances which meet the following criteria:

- are toxic for human health and for wildlife;
- remain intact in the environment for long periods of time;
- are widely distributed throughout the environment;
- bioaccumulate in fatty tissues of humans and animals.

All POPs are listed in the Stockholm Convention on Persistent Organic Pollutants[81], which was adopted on the 22nd of May 2001 in Stockholm (Sweden) and entered into force on the 17th of May 2004. The goal of this convention is to protect human health and the environment from harmful and widely distributed chemicals (exposure to POPs can lead to serious health problems including cancer). The Convention requires its parties to eliminate or reduce the release of POPs into the environment.

Initially, twelve pollutants called the "dirty dozen" were listed in the convention: aldrin, endrin, dieldrin, chlordane, toxaphene, heptachlor, mirex, hexachlorobenzene, DDT, PCB, PCDD and PCDF. They are exclusively intentionally produced organochlorinated pesticides; the only exceptions are PCDD/F, which are highly toxic impurities/by-products with varying origin.

Later, more chemicals were included into the Convention by its amendments[81] in 2009, 2011, 2013 and 2014: hexabromocyclododecane, endosulfan, chlordecone, α-HCH, β-HCH, γ-HCH, pentachlorobenzene, hexabromobiphenyl, hexabromodiphenyl ether, heptabromodiphenyl ether, perfluorooctane sulfonic acid (PFOA), its salts and perfluorooctane sulfonyl fluoride, tetrabromodiphenyl ether and pentabromodiphenyl ether.

There are also chemicals proposed for listing under the Convention which are currently under review: decabromodiphenyl ether (commercial mixture, c-decaBDE), dicofol, short-chained chlorinated paraffins, chlorinated naphthalenes, hexachlorobutadiene and pentachlorophenol.

4.2.1   Ferrates in POPs remediation

A very limited number of papers have been published concerning the reactivity of ferrates with POPs. To the best of our knowledge, there is one single study specifically on the oxidation of PFOA and PFOS by Fe(IV) and Fe(V).[82]

Oxidation of PFOA and PFOS was described last year by Yates et al.[82] They compared the oxidation ability of Fe(IV) and Fe(V) at pH 7.0 and 9.0. The maximum rate of removal obtained

was 34 % for PFOS at pH 9.0 and 23 % for PFOA at pH 7.0, both by Fe(IV). Fe(IV) had a higher ability to oxidise these compounds. When testing the presence of F^- ion, none was found. This indicated that the mineralization was either not complete or that there was an absorption/co-precipitation of F^- ion to Fe(III) particles formed during the reduction of ferrates.

5 EXPERIMENTAL PART, RESULTS AND DISCUSSION

5.1 Characteristics of the used ferrates

I worked with five different ferrates during my experiments. One was commercially available highly pure ferrate obtained from Sigma-Aldrich (hereinafter referred to as SA). Further, there were three semi-pilot scale batches of ferrates manufactured and provided by the company LAC (hereinafter referred to as LAC A, LAC B and LAC C). Finally, the last was obtained from Zhenpin Chemicals Engineering Ltd, Shanghai, China (hereinafter referred to as Zhenpin).

The used ferrates were characterized by LAC and UPOL. Mössbauer spectra provided molar fractions of the individual oxidation states of the Fe atoms. Elemental analysis was made by AAS and flame photometry. Weight fractions (Table 1) were calculated based on the elemental analysis and molar fractions. Table 1 also reveals the original oxidation state of the iron in the solid ferrate. All of the LAC ferrates were Fe(V) while the SA and Zhenpin were Fe(VI). As explained in Chapter 4.1.2, this does not have any consequence for our experiments.
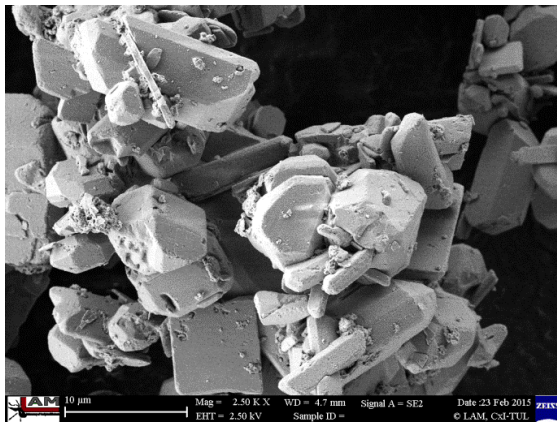
Table 1: Proportion of active ingredients

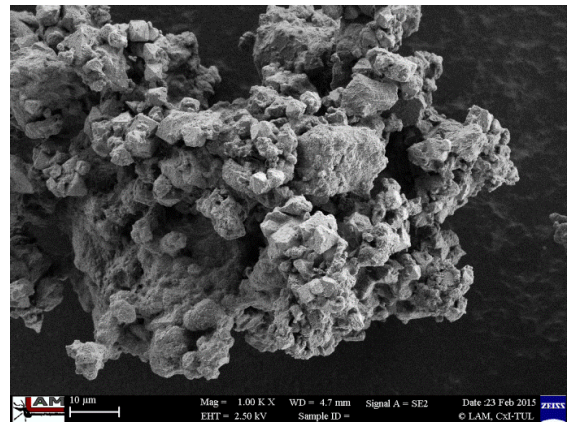| Weight fraction	SA	LAC A	LAC B	LAC C	Zhenpin
$K_3Fe(V)O_4$	-	18 ± 3 %	43 ± 3 %	22 ± 3 %	-
$K_2Fe(VI)O_4$	89 ± 3 %	-	-	-	11 ± 3 %

Ferrates were also characterized by field emission scan electron microscope FE SEM (Carl Zeiss Ultra Plus). The SEM was equipped with an EDS (Energy-Dispersive X-Ray Spectroscopy) detector (Oxford X-Max 20) which was used for assessment of local chemical composition (Table 2). Images from the electron microscope (Figure 4) correspond to the EDS results (Table 2). The SA ferrate is without doubt the purist one with significant crystals visible. LAC A and LAC B have a similar appearance appropriate to their similar EDS composition. On the other hand, the image of LAC C is very different, corresponding again to the very different amount of iron present (Table 2). The Zhenpin ferrate preparation technique is not known. Therefore, it cannot be really compared with the LAC ferrate images. The Zhenpin ferrate is also the only one which contained quite large amount of chlorine. Thus, this ferrate could not be used measuring chlorine and consequently for monitoring the degradation/mineralization of the target pollutants, which are mostly chlorinated (for an example see 5.2.3). For easier orientation, Table 2 also provides calculated (theoretical) elemental compositions of pure K_2FeO_4 and K_3FeO_4 phases.

Table 2: EDS elemental analysis (left part) and theoretical calculated compositions (right part)

Weight fraction	SA	LAC A	LAC B	LAC C	Zhenpin	K_2FeO_4 (SA and Zhenpin)	K_3FeO_4 (LAC ferrates)
K	38%	48 %	45 %	65 %	44 %	40 %	49 %
Fe	43 %	14 %	19 %	4 %	6 %	28 %	24 %
O	19 %	32 %	32 %	31 %	34 %	32 %	27 %
Cl	-	-	-	-	8 %	-	-
N	-	6 %	4 %	-	2 %	-	-
Na	-	-	-	-	6 %	-	-

SA

LAC A
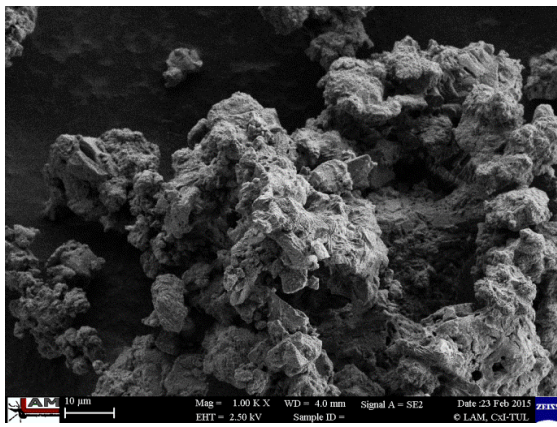
LAC B
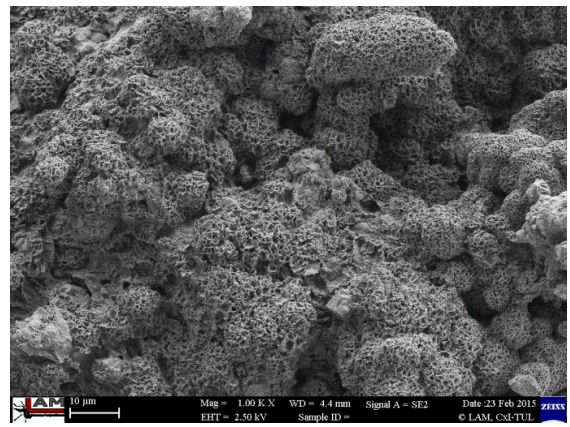
LAC C
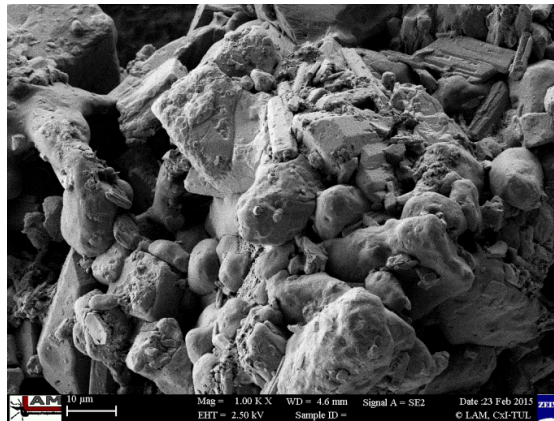
Zhenpin

Figure 4: Microscope images of the used ferrates

The results shown in tables 1 and 2 are not comparable as each technique used for measurement has a different principle. AAS determines the composition of the whole bulk unlike EDS, which assesses only the local composition. Also, the measurements were not carried out in the same time. Specifically, for example, elemental analysis of LAC ferrates was performed right after their preparation without any transportation or storage needed, but EDS analysis was performed

at our university after a longer time and after repeated opening of the storage container during use.

Elemental analysis of ferrates was performed using an ICP-OES spectrometer (Perkin Elmer Optima 2100 DV) after the decomposition of solid samples with hydrochloric acid. The results from this trace analytical method are shown in Table 3. The presence of toxic heavy metals (especially Cd, Be, As and Pb) has to be considered in the case of application into the environment.

Table 3: ICP-OES/MS analysis of the used ferrates

mg/kg	SA	LAC A	LAC B	LAC C	Zhenpin
Be	4.523	4.079	4.130	5.911	0.913
As	< 25	< 25	< 25	< 25	< 25
Cu	3.742	6.821	5.539	27.85	3.338
Cr	1081	31.93	17.55	988.7	23.50
Zn	22.85	81.58	57.36	69.81	8.081
V	< 5	9.720	9.531	14.83	< 5
Co	< 50	< 50	< 50	< 50	< 50
Ni	< 5	38.11	31.97	374.6	11.41
Pb	< 25	< 25	< 25	< 25	< 25
Cd	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5

Finally, the most important analysis of ferrates and the only really relevant result for the experiments was the content of FeO_4^{2-} in the solution after the dissolution of the solid sample, either K_2FeO_4 or K_3FeO_4. In total, 0.02 g of each solid sample was dissolved in 100 ml of demineralised water and the FeO_4^{2-} concentration was determined using spectrophotometry ($\varepsilon = 1150$ M^{-1}cm^{-1}; $\lambda = 505$ nm) after 1 minute of vigorous stirring. The pH of the solution was also measured (Table 4). The last line of Table 4 states the weight fractions of the pure ferrate phases (K_2FeO_4 or K_3FeO_4 for SA and Zhenpin, or LAC, respectively) in the whole solid sample calculated from the measured molar concentrations (the first line of Table 4). This data showed again the significant difference in purities between the particular ferrates; SA ferrate being incomparably purer than the others.

Table 4: The concentration of FeO_4^{2-} and pH after dissolution of 0.02 g in 100 ml of demineralised water

	SA	LAC A	LAC B	LAC C	Zhenpin
FeO_4^{2-} (mmol/l)	0.88	0.10	0.27	0.09	0.18
pH	9.6	10.4	10.9	10.7	10.0
fraction (w/w) of K_2FeO_4 or K_3FeO_4	87.2 %	11.9 %	32.0 %	10.7 %	17.8 %

5.2   Reactivity of ferrates with POPs

Representatives of POPs were selected for study on the basis of their relevance in the Czech Republic. Although some of the POPs were studied in model water, at least one real contaminated site does exist for HCH, PCP, PCDD/F, PeCB, HCB and PCB.

To the best of our knowledge, the below mentioned studies are the first to describe the behaviour of HCH, PCP, PCDD/F, PeCB, HCB and PCB in the presence of ferrate.

5.2.1   Hexachlorocyclohexanes

Abstract: Regarding environmental pollution, the greatest public and scientific concern is aimed at the pollutants listed under the Stockholm Convention. These pollutants are not only persistent but also highly toxic with a high bioaccumulation potential. One of these pollutants, γ-HCH, has been widely used in agriculture, which has resulted in wide dispersion in the environment. Remediation of this persistent and hazardous pollutant is difficult and remains unresolved. Of the many different approaches tested, none to-date has used ferrates. This is unexpected as ferrates are generally believed to be an ideal chemical reagent for water treatment due to their strong oxidation potential and absence of harmful by-products. In this paper, the degradation/transformation of HCHs by ferrates under laboratory conditions was studied. HCH was degraded during this reaction, producing trichlorobenzenes and pentachlorocyclohexenes as by-products. A detailed investigation of pH conditions during Fe(VI) application identified pH as the main factor affecting degradation. We conclude that ferrate itself is unreactive with HCH and that high pH values, produced by K_2O impurity and the reaction of ferrate with water, are responsible for HCH transformation. Finally, a comparison of Fe(VI) with Fe(0) is provided in order to suggest their environmental applicability for HCH degradation.

Conclusions: This paper is the first to investigate the potential use of ferrate(VI) for removing/degrading HCH pollutants. Our results indicate, however, that ferrate is not applicable for HCH removal under the conditions used, the high pH of the ferrate(VI) solution probably causing HCH transformation rather than the high oxidation potential of the solution. Under alkaline pH experimental conditions, HCHs were transformed into TCBs (with PCCHs as intermediates), which both have similar levels of toxicity and persistence in natural systems. In comparison, HCH concentrations decreased after the addition of iron in the form of nZVI, with benzene and ChB forming as degradation products.

Citation: Homolková, M., Hrabák, P., Kolář, M., Černík, M. Degradability of hexachlorocyclohexanes in water using ferrate (VI). *Water Sci. Technol.* **71,** 405–411 (2015)

5.2.2 Chlorophenols

Abstract: The production and use of chlorophenolic compounds in industry has led to the introduction of many xenobiotics, among them chlorophenols (CPs), into the environment. Five CPs are listed in the Priority Pollutant list of the U.S. EPA, with pentachlorophenol (PCP) even being proposed for listing under the Stockholm Convention as a persistent organic pollutant (POP). A green procedure for degrading such pollutants is greatly needed. The use of ferrate could be such a process.

This paper studies the degradation of CPs (with an emphasis on PCP) in the presence of ferrate both in a spiked demineralized water system as well as in real contaminated groundwater. Results proved that ferrate was able to completely remove PCP from both water systems. Investigation of the effect of ferrate purity showed that even less pure and thus much cheaper ferrate was applicable. However, with decreasing ferrate purity the degradability of CPs may be lower.

Conclusions: The present paper is the first to study the applicability of FeO_4^{2-} for PCP degradation/removal in water. The results proved that ferrate could be suitable for such an application, as all of the CPs, including the most persistent PCP, were completely removed. Total degradation did indeed take place; the removal was not caused by sorption on the iron precipitation as the whole content of the reactors was extracted into hexane. This degradation was confirmed both in the spiked water system as well as in real complex contaminated water from a former pesticide production area. Furthermore, utilization of less pure ferrates was also discussed. We assume that the use of ferrate for remediation of PCP contaminated water could be considered as a green process. Further work needs to be done to establish the kinetic constants of CP degradation by ferrate. The degradation products along with the degradation pathway also remain to be found.

Citation: Homolková, M., Hrabák, P., Kolář, M., Černík, M. Degradability of pentachlorophenol using ferrate(VI) in contaminated groundwater. *Environ. Sci. Pollut. Res.* **23**, 1408-1413 (2016)

5.2.3 Pentachlorophenol

Abstract: Pentachlorophenol (PCP) is a persistent pollutant which has been widely used as a pesticide and a wood preservative. As PCP is toxic and is present in significant quantities in the environment there is considerable interest in elimination of PCP from waters. One of the promising methods is the application of ferrate.

Ferrate is an oxidant and coagulant. It can be applied as a multi-purpose chemical for water and wastewater treatment as it degrades a wide range of environmental pollutants. Moreover, ferrate is considered a green oxidant and disinfectant.

This study focuses on the kinetics of PCP degradation by ferrate under different pH conditions. The formation of degradation products is also considered.

The second-order rate constants of the PCP reaction with ferrate increased from 23M-1s-1 to 4948 M-1s-1 with a decrease in pH from 9 to 6. At neutral pH the degradation was fast indicating that ferrate could be used for rapid removal of PCP.

The total degradation of PCP was confirmed by comparing the initial PCP molarity with the molarity of chloride ions released. We conclude no harmful products are formed during ferrate treatment as all PCP chlorine was released as chloride. Specifically, no polychlorinated dibenzo-p-dioxins and dibenzofurans were detected.

Conclusions: In this paper the kinetics of PCP degradation by ferrate (VI) in water were investigated. Second-order reaction rates were determined under different pH conditions from pH 6 to pH 9. The rate constant decreased logarithmically with pH according to the following empirical relationship: k $(M^{-1}s^{-1})$ = $5x10^8$ exp(-1.866 pH). At lower pH values the reaction was significantly faster owing to the greater oxidation potential of the protonated form of Fe(VI). As the degradation is sufficiently fast at neutral pH conditions ($k > 10^3\,M^{-1}s^{-1}$), ferrate oxidation may be a suitable, effective and 'green' process for the treatment of water contaminated by this potentially harmful compound (PCP). The sustainability of this treatment was also confirmed by studying the degradation products of PCP. We confirmed the total degradation of PCP and the release of the associated chlorine as chloride anions under our reaction conditions. Furthermore, no detectible concentrations of PCDD/F and PCB were produced during the reaction, which was confirmed by GC-HRMS. Thus, no harmful products are formed from PCP during the reaction and therefore we conclude that there are no potentially toxic effects during ferrate oxidation. The mechanism of PCP degradation by Fe(VI) is the subject of further research.

5.2.4 PCDD/F

Abstract: Due to the extreme toxicity of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F), the remediation of PCDD/F aquifer source zones is greatly needed; however, it is very difficult due to their persistence and recalcitrance.

The potential degradability of PCDD/F bound to a real matrix was studied in five systems: iron in a high oxidation state (ferrate), zero-valent iron nanoparticles (nZVI), palladium nanopowder (Pd), a combination of nZVI and Pd, and persulfate (PSF). The results were expressed by comparing the total toxicity of treated and untreated samples. This was done by weighting the concentrations of congeners (determined using a standardized GC/HRMS technique) by their defined toxicity equivalent factors (TEF).

The results indicated that only PSF was able to significantly degrade PCDD/F. Toxicity in the system decreased by 65% after PSF treatment. Thus, we conclude that PSF may be a potential solution for in-situ remediation of soil and groundwater at PCDD/F contaminated sites.

Conclusions: In this paper the potential degradation of PCDD/F bound to a real matrix was studied by five different oxidants and reductants commonly used for in-situ remediation, i.e. Fe(VI), nZVI, Pd, Pd+nZVI and PSF. We conclude that only the treatment by sulfate and hydroxyl radicals formed in the heat-activated PSF system exhibited a significant decrease in the PCDD/F concentrations. This decrease was 65 % when comparing the total toxicity of the base and the treated samples. Thus, PSF activated at 50 °C may be used for the remediation of aquifers contaminated by these priority pollutants. Future research should be devoted to studying wider range of activation temperatures, whereby the lower ones are of much technological interest. Other PSF activation procedures (electroactivation, alkaline activation or hydrogen peroxide activation as examples) have also a potential to create strongly mineralising conditions applicable for PCDD/F degradation.

Citation: Hrabák, P., Homolková, M., Waclawek, S., Černík, M. Chemical degradation of PCDD/F in contaminated sediment. *Ecol. Chem. Eng. S.* **23**, 473-482 (2016)

5.2.5 Penta- and hexachlorobenzene

To test the ability of ferrates to degrade PeCB and HCB, two separate saturated water solutions containing these contaminants were prepared and SA ferrate was used. Experiments with both POPs were made in triplicate and included base samples (e.g. samples with no ferrate presented), samples treated with low (0.13 mM) and with high (0.33 mM) ferrate doses and two sets of samples, which revealed the effect of the matrix (the content of these reactors was the same as in the case of ferrate-treated samples; only PeCB or HCB was added after the total ferrate decomposition). The content of PeCB and HCB was determined using GC-MSMS using two different methods. The first was liquid-liquid extraction into hexane followed by liquid injection and the second was direct SPME technique. In both cases, γ-HCH D6 was used as the internal standard.

The results showed no difference between the base samples, the samples treated with both doses of ferrates and the samples which revealed the effect of the matrix. Thus, we conclude that ferrates are not applicable for PeCB or HCB removal as no decrease in their concentration was observed (data not shown).

5.2.6 Polychlorinated biphenyls

Out of 209 structurally possible congeners, seven have been selected by EPA as indicative for qualification in environmental matrices: PCB 28, 52, 101, 118, 138, 153 and 180. The reactivity of these PCBs with ferrates was determined in real contaminated water. Three different concentrations of SA ferrate were applied to the contaminated water. After liquid-liquid extraction, the concentration of PCB in these samples was compared with the concentration in fresh contaminated water using GC-MSMS.

The results showed no difference between the samples. Thus, we conclude that ferrates are not applicable for PCB removal as no decrease in their concentration was observed (data not shown).

6 CONCLUSION

When taking into account the exceptional features of ferrates – their high redox potential, multimodal action (oxidation, coagulation, and disinfection), non-toxic by-products and final products, but also their high price and storage-stability problems, it is clear that it will be difficult for ferrates to become a common water treatment chemical for ordinary pollutants. Rather, their practical utilization could be expected in the field of special industrial wastewater or the elimination of the most problematic compounds, among which POPs certainly belong.

The reactivity of ferrate with HCHs is discussed in the publication "Degradability of hexachlorocyclohexanes in water using ferrate (VI)[83]" by Homolková, Hrabák, Kolář, and Černík; published in 2015 in the journal Water Science and Technology. A detailed investigation of pH conditions is a part of this study, as they influenced the results significantly. Furthermore, a comparative study of HCH with nZVI particles was also performed. Degradation products together with intermediates were found for both extreme iron valences. Very briefly, ferrate itself is unreactive with HCHs and thus not applicable for their removal/degradation. The transformation of HCHs into trichlorobenzenes in the presence of ferrate is caused by increased pH. On the other hand, nZVI particles, showed a promising reactivity towards HCHs (not the topic of this thesis).

Ferrates are applicable for PCP and for chlorophenol removal in general, which has been proven in both a spiked water system as well as in real contaminated groundwater. This degradation was fast and full. Furthermore, an investigation of the effects of the dose and purity of the ferrates on their applicability was also discussed. These results were described in the article "Degradability of chlorophenols using ferrate(VI) in contaminated groundwater"[84] by Homolková, Hrabák, Kolář, and Černík; published in 2016 in the journal Environmental Science and Pollution Research.

A study of the kinetics of PCP degradation by ferrates under different pH conditions was also made. Furthermore, it was found that there is a total mineralization of PCP to chloride anions and carbon dioxide in this reaction. The related publication "A study of the reaction of ferrate with pentachlorophenol – kinetics and degradation products"[85] by Homolková, Hrabák, Graham, and Černík was published in 2017 in the journal Water Science and Technology.

The potential degradability of the highest priority pollutants, PCDD/F, bound to a real matrix was studied in five systems: iron in a high oxidation state (ferrate), zero-valent iron nanoparticles (nZVI), palladium nanopowder (Pd), a combination of nZVI and Pd, and persulfate (PSF). Details of the experiment together with the results are described in the paper "Chemical degradation of PCDD/F in contaminated sediment"[86] by Hrabák, Homolková, Waclawek and Černík, which was published in 2016 in the journal Ecological Chemical Engineering S.

The results indicated that only PSF was able to significantly degrade PCDD/F. Thus, we conclude the inapplicability of ferrates for PCDD/F degradation.

In addition to the published results, the reactivity of ferrates with penta- and hexachlorobenzene and PCB was also studied. In all three cases, no decrease in the concentration of POPs in the presence of ferrates was observed. Thus, we conclude that ferrates are not applicable for their removal.

To summarize, the applicability of ferrates for the removal of three individual persistent organic pollutants (PCP, PeCB and HCB) and three groups of POPs (HCHs, PCDD/F and PCBs) was studied in detail. HCHs, PCDD/F, PeCB, HCB and PCB are unreactive with ferrates; on the other hand, PCP is very well degradable.

To date, four articles[83,84, 85, 86] covering this topic have been accepted and published in impact journals.

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Degradability of hexachlorocyclohexanes in water using ferrate (VI)

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ABSTRACT

Regarding environmental pollution, the greatest public and scientific concern is aimed at the pollutants listed under the Stockholm Convention. These pollutants are not only persistent but also highly toxic with a high bioaccumulation potential. One of these pollutants, γ-hexachlorocyclohexane (γ-HCH), has been widely used in agriculture, which has resulted in wide dispersion in the environment. Remediation of this persistent and hazardous pollutant is difficult and remains unresolved. Of the many different approaches tested, to date, none has used ferrates. This is unexpected as ferrates are generally believed to be an ideal chemical reagent for water treatment due to their strong oxidation potential and the absence of harmful by-products. In this paper, the degradation/transformation of HCHs by ferrates under laboratory conditions was studied. HCH was degraded during this reaction, producing trichlorobenzenes and pentachlorocyclohexenes as by-products. A detailed investigation of pH conditions during Fe(VI) application identified pH as the main factor affecting degradation. We conclude that ferrate itself is unreactive with HCH and that high pH values, produced by K_2O impurity and the reaction of ferrate with water, are responsible for HCH transformation. Finally, a comparison of Fe(VI) with Fe(0) is provided in order to suggest their environmental applicability for HCH degradation.

Key words | degradability, ferrate, Fe(VI), hexachlorocyclohexane, persistent organic pollutants

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INTRODUCTION

Hexachlorocyclohexanes (HCHs), along with chlorobenzenes (ChBs), chlorophenols and dichlorodiphenyltrichloroethane, are organochlorinated pesticides (OCPs), most of which are listed under the Stockholm Convention and its updates as persistent organic pollutants (POPs). There has been considerable public and scientific concern over environmental pollution with POPs as, once released into the environment, they resist all natural means of degradation (physical, biological, chemical and photochemical). Exposure to POPs can cause cancer, reproductive defects, neurobehavioural abnormalities and endocrine and immunological disorders (Mrema *et al.* 2013).

HCH exists in nine stereoisomeric forms, the most common being α-HCH, β-HCH, γ-HCH and δ-HCH. γ-HCH, also known as lindane, has been used as both an agricultural insecticide and a pharmaceutical and veterinary treatment for lice and scabies (Abhilash & Singh 2010). It is estimated that around 600,000 tonnes of lindane were produced globally over the last century, the vast majority being

used in agriculture (Mrema *et al.* 2013). The World Health Organisation classifies lindane as being 'moderately hazardous' and the use of technical HCH was banned between the 1970s and 1980s. HCH was further listed under the Stockholm Convention in 2009. Although the use of lindane as a pesticide was prohibited over 30 years ago, background concentrations can still be found in water and soil (Ren *et al.* 2006).

In addition to the issue of lindane pollution, there are concerns related to the HCH ballast isomers α-HCH and β-HCH, which are by-products of lindane production and lack its insecticidal properties. Both isomers are notably more toxic than lindane itself. In the 1940s and 1950s, prior to the industrial application of the isomerisation procedure, lindane producers stockpiled ballast isomers in open heaps, which led to both soil and groundwater contamination. Furthermore, β-HCH shows higher levels of bioaccumulation than other isomers; hence, β-HCH contributes significantly to the total HCH body burden.

Pesticides are traditionally removed from contaminated ground/wastewater by coagulation, flocculation, membrane separation or adsorption on activated carbon (Nitoi *et al.* 2013). In fact, these technologies do not degrade the contaminants themselves but transfer them onto other matrices, which must then be further treated themselves. One example of a common degradation procedure is that of catalytic reductive dehydrochlorination, which yields benzene (C_6H_6) as the major final product. While there are many publications on reductive transformation and degradation of HCHs (e.g. Wang *et al.* 2009; Singh *et al.* 2012), there are relatively few concerning oxidation methods (Cao *et al.* 2008), and none on the use of ferrates.

Ferrates, the higher oxidation states of iron Fe(IV, V and VI) have attracted much interest in recent years due to their involvement in the treatment of a diverse range of common environmental pollutants (Sharma *et al.* 2008b; Al-Abduly & Sharma 2014). Potassium ferrate (K_2FeO_4) is a strong oxidant, disinfectant and coagulant that has a stronger oxidation potential under moderately acidic pH conditions than any other chemical commonly used for wastewater treatment (chlorine, hypochlorite, chlorine dioxide, ozone, hydrogen peroxide, dissolved oxygen or permanganate). Furthermore, there are no known side-effects and no potentially harmful ferrate by-products from the treatment process. Chlorination, for example, which has been the most commonly used wastewater treatment technology since the early 1900s, produces carcinogenic by-products such as trihalomethanes and haloacetic acids (Heller-Grossman *et al.* 1993). Other by-products of chlorination and their health effects have been further summarised by Skaggs *et al.* (2008). In comparison, the by-product of ferrate oxidation is the ferric ion Fe(III), which is environmentally benign and a micronutrient for plant life:

$$2\,FeO_4^{2-} + 5\,H_2O = 2\,Fe^{3+} + 3/2\,O_2 + 10\,OH^- \qquad (1)$$
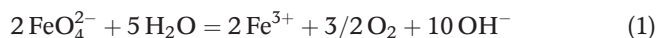
Conversely, ferrates are the most expensive oxidant and require very special handling. Despite this, ferrates are presently considered a highly promising 'green' water treatment oxidant, disinfectant and coagulant (Filip *et al.* 2011; Prucek *et al.* 2013).

There have been many recent studies on the use of ferrates in the degradation of a wide range of organic (e.g. Sharma 2013) and inorganic pollutants (e.g. Sharma 2011) in aquatic environments, and their use in water and wastewater disinfection (e.g. Bandala *et al.* 2009), treatment of sewage sludge (e.g. Jiang *et al.* 2006), removal of humic substances (e.g. Jiang 2007) and treatment of emerging organic pollutants such as endocrine disrupting chemicals and pharmaceuticals and personal care products (Lee *et al.* 2005; Sharma *et al.* 2008a, 2013). However, only a limited amount of work has been published focusing on the removal of OCPs or POPs (Singh *et al.* 1985), potentially the most hazardous pollutants.

This study represents part of a wider feasibility study for the remediation of complex contamination of water from former pesticide production areas. As stated above, the number of previous studies examining degradability of POPs using ferrates is limited, despite ferrates being considered by many authors to be an ideal wastewater treatment reagent and POPs being priority pollutants. The present study examines the applicability of Fe(VI) for HCH degradation/removal and especially the role of pH. Furthermore, for comparison, zero-valent iron nanoparticles (nZVI) were used to assess the effect of a similar amount of Fe at opposite extremes of valence (Fe^0). HCH degradation was expected in nZVI systems in accordance with a previous study (Wang *et al.* 2009).

MATERIALS AND METHODS

Chemicals

The potassium ferrate (produced as part of our research project) used in our study had a composition (as determined through a combination of ^{57}Fe Mössbauer spectroscopy and atomic absorption spectroscopy) of 83.6 wt% K_2FeO_4, 6.5 wt% Fe_2O_3 and 9.9 wt% potassium oxides with traces of silicon, aluminium and zirconium. Stock solutions (0.5–2 mM) of Fe(VI) were prepared by dissolving the solid sample in cooled demineralised water (obtained using a PURELAB flex system (ELGA LabWater, Prague, Czech Republic)). Owing to the inhomogeneity of the ferrate material, it was not possible to calculate precise ratios in advance; hence, final concentrations of the Fe(VI) stock solutions were calculated retrospectively after photometric measurement. For this reason, the ratios in repeat experiments varied slightly. All of the Fe(VI) stock solutions were used within 15 min of preparation.

A saturated stock solution of HCH was prepared by dissolving standard HCH (isomer mixture α:β:γ:δ = 1:1:1:1; purity >99.3%; Fluka, Sigma–Aldrich Co., Prague, Czech Republic) in demineralised water. This was filtered through a 0.45 μm filter after vigorous stirring for 3 days. The stock solution was then stored in a refrigerator at 5 °C.

Standard NANOFER 25P nZVI (NANO IRON, s.r.o., Olomouc, Czech Republic) was used in the form of a dry powder preserved in an inert nitrogen atmosphere. The particles were without surface modification and had an average size of 50 nm, average surface area of 20–25 m^2/g and a narrow size distribution of 20–100 nm. The content of iron was high, ranging between 80 and 90 wt%. An aqueous suspension of Fe(0) was prepared from the powder at a ratio of 1:4 nZVI:water, which yielded a suspension with an nZVI content of 0.2 g Fe(0)/1 ml.

Methods

Each experiment was performed in a 100 ml reaction flask. The specified amount of demineralised water or H_3BO_3/NaOH buffer (depending on the experiment) was placed into the flask, spiked with 10 ml of HCH stock solution and the required amount of ferrate stock solution was added. The total reaction volume was always 50 ml. Unless stated otherwise, the solutions were extracted (shaking for 30 min at 150 rpm) with 10 ml of hexane the following day. Each set of samples included control and base samples. The controls were treated in the same way as the samples (same composition and simultaneous extraction) but without addition of the ferrate in order to distinguish the influence of pH or time from the influence of the ferrate. The base samples comprised demineralised water spiked with HCH and were extracted straight after preparation to determine the initial concentration of HCH without pH or time influence. All of the experiments were undertaken in triplicate and at ambient temperature.

Experiments with nZVI were performed under the same experimental set-up. Two different approaches for nZVI dosing were chosen, the first being to dose approximately the same molar amount of nZVI into the reactor as the Fe(VI) dose, i.e., 5 µmol (=100 µmol/l). As this amount was very small, a second set of reactors was prepared using a more commonly used concentration of nZVI, i.e., 1 g/l. The experiments were performed in duplicate in demineralised water with no pH adjustment, but with a constant watch on pH evaluation. In all of the experiments (FeVI and nZVI) HCH and ChB (including benzene) were measured.

Analytical methods

HCH and higher chlorinated ChB (tri-, tetra-, penta- and hexachlorobenzene) were determined in hexane extracts using a Trace 1310 gas chromatograph fitted with a triple quadrupole tandem TSQ 8000 mass spectrometry detector

(Thermo Scientific TM, Pragolab, Prague, Czech Republic). Unknown peaks of the mass spectra were compared with the National Institute of Standards and Technology library. In some cases, peaks were identified as potential reaction by-products. Less than tri-chlorinated benzenes (dichlorobenzenes, chlorobenzene and benzene) were quantified by the static head-space method using a CP-3800 gas chromatograph with a Saturn 2200 ion trap mass spectrometry detector (Varian, Amedis, Prague, Czech Republic). Fe(VI) concentrations were determined using a Lambda 35 UV/VIS absorption spectrometer (PerkinElmer Instruments, PE Systems, Prague, Czech Republic) with molar absorptivity of 1,150 $M^{-1} cm^{-1}$ at 505 nm (Licht *et al.* 2001). Measurements of pH were carried out using a pH50 pH meter (Giorgio Bormac, Chromservis, Prague, Czech Republic), which was calibrated using standard pH 4.01, 7.00 and 10.01 buffers.

RESULTS AND DISCUSSION

HCH reactivity with ferrate

A preliminary experiment was conducted to examine whether transformation/degradation of HCH does occur in an HCH/Fe(VI) system. Ferrate was added to a solution containing demineralised water (adjusted to pH 9 with NaOH) and the HCH isomers. To investigate the influence of ferrate dose, two different theoretical Fe(VI):HCH molar ratios of 10:1 and 30:1 were used. Two repeats of the experiment produced molar ratios of 7.6:1, 10.3:1, 23:1 and 34.2:1, respectively. In addition to HCH, the concentration of ChB was also monitored as previous studies have shown that ChB can form as a by-product of HCH at an alkaline pH (Ren *et al.* 2006). The results confirmed a decrease in HCH in the HCH/Fe(VI) system accompanied by an increase in ChB with an increasing dose of ferrate (Figure 1).

The comparable concentrations of base and control samples indicated that the HCH concentration does not change without the presence of ferrate. Two trichlorobenzene isomers (TCB) were found in this system, namely 1,2,4-trichlorobenzene and 1,2,3-trichlorobenzene, with the former dominating.

Because the unbuffered, aqueous ferrate solution tends to increase its pH value (Equation (1)), a further step was taken to distinguish the role of ferrate and the particular influence of increased pH. A second experiment was conducted wherein three sets of reactors were prepared containing water buffered to pH 9, 10 or 11 with no ferrate
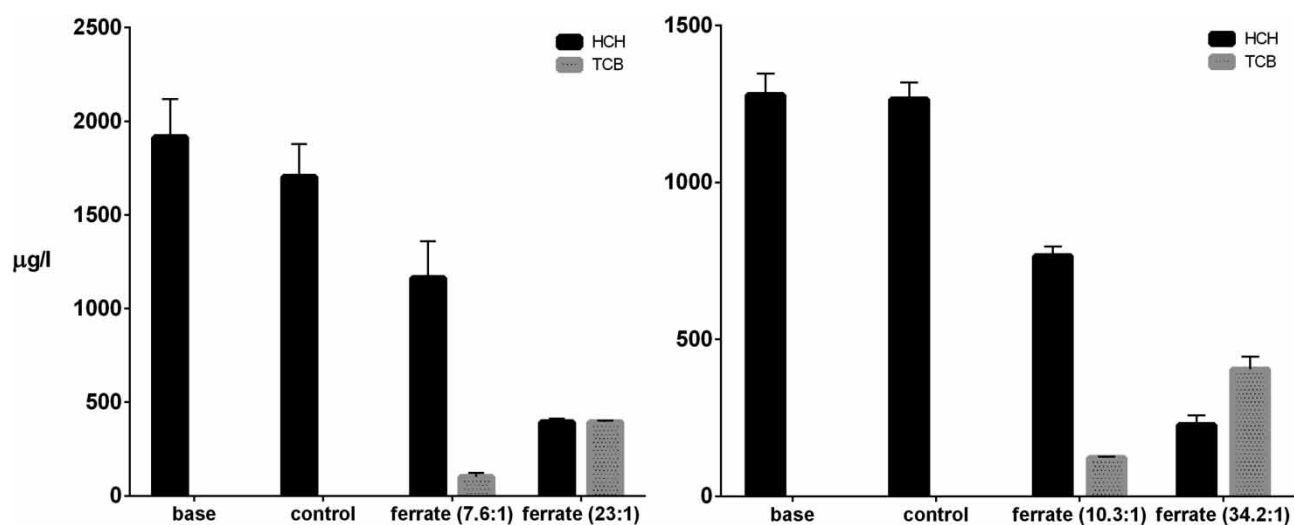
Figure 1 | Concentration of HCH and TCB after addition of different amounts of FeO_4^{2-} (mean + standard deviation; μg/l).
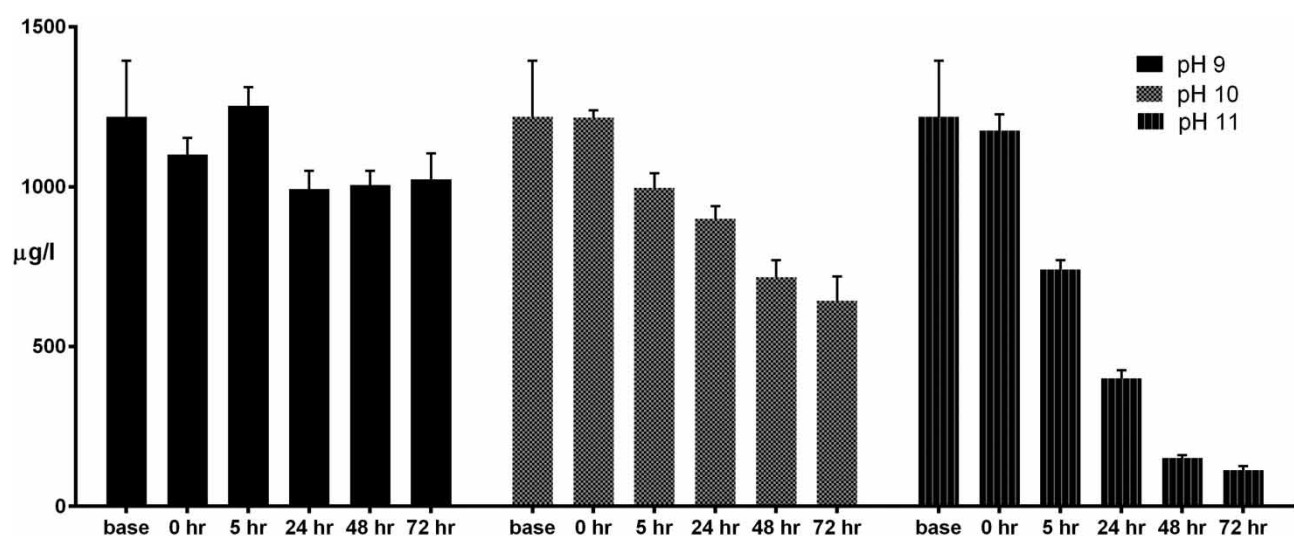

Figure 2 | Concentration of HCH over time at pH 9, 10 or 11 with no ferrate added (mean + standard deviation; μg/l).

added. Concentrations of HCH and ChB were measured after 0, 5, 24, 48 and 72 h (Figure 2). In the pH 10 and pH 11 reactors the concentration of HCH decreased significantly over time, accompanied by an increase in TCBs (1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene; data not shown), the trend being most obvious at pH 11. A decrease in the concentration of HCH was not confirmed at pH 9 (Figure 2). These results led to the assumption that the HCH transformation/degradation shown in Figure 1 may have been a consequence of increased pH in the reaction system only.

As there was no significant transformation of HCH at pH 9 (Figure 2) this pH appeared suitable for other experiments with ferrate as any transformation/degradation

observed would have been caused by the ferrate itself. The comparison of the control with the test solution with a molar ratio of ferrate to HCH of 17:1, both buffered to pH 9, indicated no decrease in HCH (Figure 3, left). This suggested that pH, and not ferrate, may be the main driver in the HCH degradation observed in Figure 1.

As the ferrate reactivity is known to be higher at lower pH levels (Lee *et al.* 2004), it was anticipated that HCH degradation would increase under more acidic conditions. To confirm this, the previous experiment was repeated under neutral (pH 7) and slightly acidic (pH 5) conditions. The ferrate to HCH molar ratio remained the same, i.e., 17:1. Each reactor (containing buffered water and HCH) was stirred vigorously because the ferrate reacts instantly
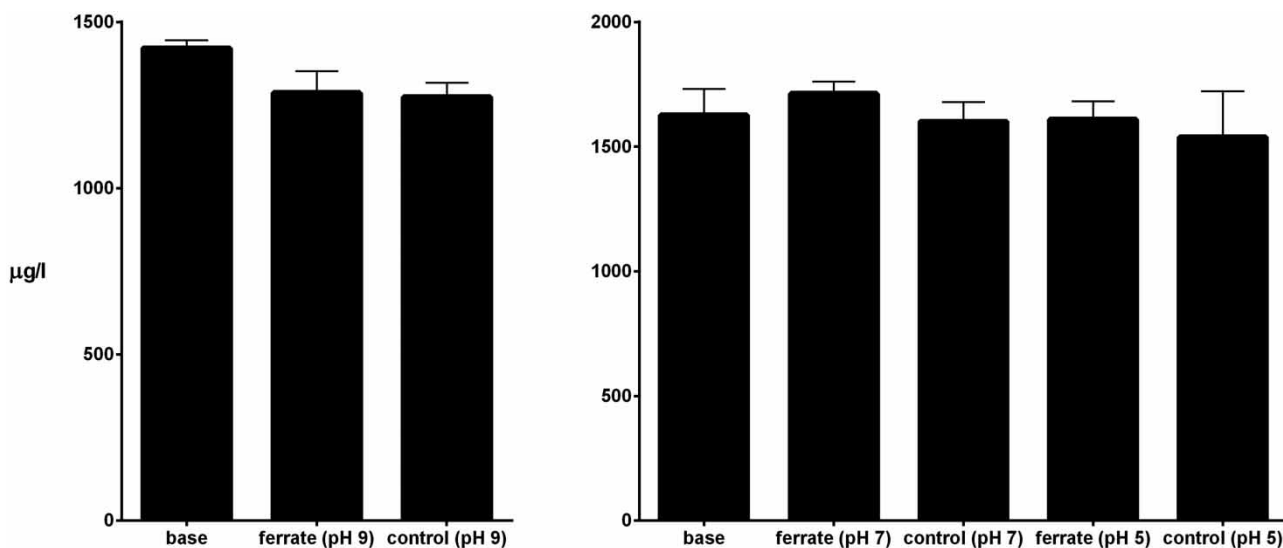
Figure 3 | Concentration of HCH in the base and the control samples as well as in the ferrate treated solutions at pH 5–9 (mean + standard deviation; μg/l).

in this pH range. For the same reason the ferrate stock solution was added gradually (one-tenth of the volume added at a time). The results (Figure 3, right) indicated no degradation of HCH and no formation of TCBs or other ChBs.

Briefly summarised, the degradation/transformation of HCH in the presence of ferrate was examined under a wide range of buffered pH values. There was no degradation/transformation under acidic, neutral or slightly basic conditions (pH 5, 7 and 9). The only HCH degradation/transformation occurred in the unbuffered ferrate system. The same degradation/transformation was observed without ferrate presence due to the increased pH values (pH 10 and 11). It may be concluded, therefore, that the high pH and not the ferrate was the driver of the HCH transformation in the ferrate system.

While determining the concentration of target analytes in the hexane extracts, three unknown peaks were found in the chromatograms, whose amounts increased with increasing pH. They were identified as pentachlorocyclohexene (PCCH) isomers. We assume that HCH transforms into TCB, whereby PCCHs are the transformation intermediates and no other ChB or benzene are produced in any phase of this pH driven reaction.

HCH reactivity with nZVI

Unlike in the ferrate system, only a minor pH shift was observed during the reaction of the HCH with nZVI. This suggested that the HCH should not have been influenced by pH in the same manner as in the case of the

ferrates. The results of the nZVI experiments indicated a degradation of HCH (Figure 4). Benzene and chlorobenzene were found in this system as products of reductive dechlorination.

Owing to the slow kinetics of the nZVI degradation of chlorinated hydrocarbons reported previously (Filip *et al.* 2007), only a small decrease in the concentration of HCH was observed during the experimental run, which was fixed to 24 h, similarly to the oxidation experiment. This is also the reason why no significant differences between the two nZVI concentrations were observed. It is clear that Fe(0) rather than Fe(VI) reacts with the HCH and has the potential to be applied to the HCH-contaminated matrices.
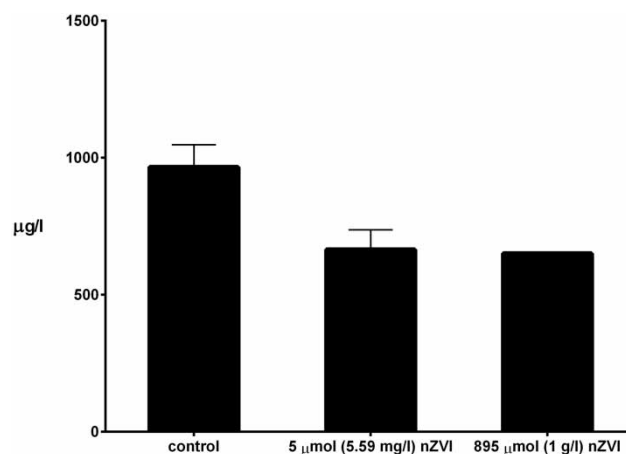
Figure 4 | Concentration of HCH after adding different amounts of nZVI (mean + standard deviation).

CONCLUSIONS

This paper is the first to investigate the potential use of ferrate (VI) for removing/degrading HCH pollutants. Our results indicate, however, that ferrate is not applicable for HCH removal under the conditions used, the high pH of the ferrate (VI) solution probably causing HCH transformation rather than the high oxidation potential of the solution. Under alkaline pH experimental conditions, HCHs were transformed into TCBs (with PCCHs as intermediates), which both have similar levels of toxicity and persistence in natural systems. In comparison, HCH concentrations decreased after the addition of iron in the form of nZVI, with benzene and ChB forming as degradation products.

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RESEARCH ARTICLE

Degradability of chlorophenols using ferrate(VI) in contaminated groundwater

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Abstract The production and use of chlorophenolic compounds in industry has led to the introduction of many xenobiotics, among them chlorophenols (CPs), into the environment. Five CPs are listed in the priority pollutant list of the U.S. EPA, with pentachlorophenol (PCP) even being proposed for listing under the Stockholm Convention as a persistent organic pollutant (POP). A green procedure for degrading such pollutants is greatly needed. The use of ferrate could be such a process. This paper studies the degradation of CPs (with an emphasis on PCP) in the presence of ferrate both in a spiked demineralized water system as well as in real contaminated groundwater. Results proved that ferrate was able to completely remove PCP from both water systems. Investigation of the effect of ferrate purity showed that even less pure and thus much cheaper ferrate was applicable. However, with decreasing ferrate purity, the degradability of CPs may be lower.

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Introduction

The group of chlorophenols (CPs) comprises 19 aromatic chlorinated congeners. They were first synthesized in the eighteenth century and were later extensively used due to their antiseptic properties. As their utilization has been replaced by more effective chemicals, less chlorinated CPs are of a limited use today (Exon 1984). In the 1930s, pentachlorophenol (PCP) started to be used as a wood preservative (Stockholm Convention on POPs, http://chm.pops.int/). Since then, not only PCP but also other CPs have been used worldwide and extensively in agriculture and industrial and domestic applications not only as wood preservatives but also as fungicides, bactericides, herbicides and insecticides and as precursors in the synthesis of other chemicals (Olaniran and Igbinosa 2011). PCP was commonly used in paper and pulp mills until the 1970s when its use was banned due to its toxic effects on aquatic species (Exon 1984). Nowadays, PCP utilization is mostly prohibited or restricted; however, it continues to be used in Canada, Mexico and the USA as a wood preservative (Stockholm Convention on POPs, http://chm.pops.int/).

When advanced analytical techniques were developed, the widespread distribution of CPs was revealed in the environment (soil, water and air samples, food products, human and animal tissues and body fluids), even in remote areas (e.g. PCP was detected in the tissues of polar bears and ringed seals), originating mostly from its previous heavy use (Exon 1984). However, it was discovered that CPs can also form spontaneously in drinking and wastewaters within chlorination during the disinfection and deodorization process. Degradation of other chlorinated xenobiotics like penta- or hexachlorobenzene (HCB), polychlorinated biphenyls (PCB) or hexachlorocyclohexane (lindane, HCH) can also produce PCP residues (Exon 1984; Stockholm Convention on POPs, http://chm.pops.int/). It was even found that technical PCP can contain persistent organic

pollutant (POP) contaminants like chlorinated dimers such as dibenzo-*p*-dioxin or dibenzofurans, PCBs, or HCB (Stockholm Convention on POPs, http://chm.pops.int/). In addition, chlorinated dimers are formed during the incineration of wastes in the presence of PCP compounds (Stockholm Convention on POPs, http://chm.pops.int/).

Chlorophenolic compounds persist in the environment as they are recalcitrant to biodegradation. They bioaccumulate in aquatic organisms after being easily transported through the cell membrane due to their lipophilicity. Furthermore, they possess a potential carcinogenic and mutagenic activity and toxicity and therefore are considered harmful for human health (Olaniran and Igbinosa 2011). Growing knowledge of these compounds made governments regulate them. Six chlorophenols (PCP, 2,4, 6- and 2,4,5-trichlorophenols, tetrachlorophenol, 2,4,-dichlorophenol and 2-chlorophenol) are nowadays listed in The Priority List of Hazardous Substances (Agency for Toxic Substances & Disease Registry, www.atsdrcdc.cdc.gov/spl). The tendency of CPs to bioconcentrate increase with its increasing chlorination due to a reduction in vapour pressure, an increase in boiling point and a reduction of water solubility (Olaniran and Igbinosa 2011). Therefore, it is not surprising that PCP, which has all five possible chlorines in its molecule, is the most hazardous CP congener and is therefore proposed for listing under the Stockholm Convention as a POP. A green process for degrading such pollutants from water and generally from the environment is greatly needed.

CPs can be generally degraded both by chemical reduction and by oxidation (Hou et al. 2011). Focusing further on oxidation, enzyme-catalysed oxidation of CPs was reported in the literature (Bollag et al. 2003; Olaniran and Igbinosa 2011); application of advanced oxidation processes (AOPs), for example degradation of PCP by ozone or Fenton system, were described by Benoitguyod et al. 1994 and Oturan et al. 2001, respectively. Degradation of CPs by higher oxidation states of iron, ferrates, has been described for some of the less-chlorinated congeners (Graham et al. 2004; Lee et al. 2005), but there is no available study on such degradation in the case of the most harmful one, PCP.

Ferrates are higher oxidation states of iron. Three forms are currently being studied for remedial utilization, namely Fe(IV), (V), and (VI). The first two forms are very unstable and disproportionate immediately in water to Fe(VI) and Fe(III) (Wahl et al. 1956; Kokarovt et al. 1972; Jeannot et al. 2002). Water decomposition of FeO_4^{2-} is significantly slower and can be described by the Eq. (1) (Jiang and Lloyd 2002; Sharma 2002).

$$4\ FeO_4^{2-} + 10\ H_2O = 4\ Fe(OH)_3 + 3\ O_2 + 8\ OH^- \quad (1)$$
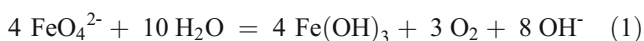
Ferrate(VI) ion, FeO_4^{2-}, is a very strong oxidant. Fe(VI) possesses a high one-electron oxidation potential (Tiwari and Lee 2011; Jiang 2014). Ferrates are applicable for degradation

of water pollutants—both organic and inorganic impurities as well as endocrine disrupting compound (EDCs) (Jiang et al. 2005; Sharma 2011; Sharma 2013). Furthermore, ferrate can be used for the disinfection of the water bodies (pathogens, bacteria, viruses) (Gombos et al. 2012). Also, the reactions (1)–(3) indicate a production of Fe(III) which serves as a coagulant/flocculant to remove non-degradable impurities (heavy metal toxic ions, radionuclides) (Filip et al. 2011). Keeping in mind these basic properties, ferrate is a multi-purpose water treatment chemical for the oxidation, coagulation and disinfection of water in a single dosing and mixing unit process (Tiwari and Lee 2011; Jiang 2014). Moreover, its principal decomposition product in redox reaction is non-toxic Fe(III) (Eq. (1)) and, as far as we know, the problematic by-products associated with the currently used chemicals such as free chlorine, chloramine or ozone are not created during treatment (Heller-Grossman et al. 1993; Richardson 2003; Skaggs et al. 2008; Zhou et al. 2009; Tiwari and Lee 2011; Han et al. 2014).

The present study examined the applicability of FeO_4^{2-} for PCP degradation/removal both from spiked water as well as from complex contaminated groundwater from a former pesticide production facility. In the case of the real groundwater, not only the concentration of PCP was monitored but also five other CPs, namely 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,3-dichlorophenol (diCP), 2,4,6-trichlorophenol (triCP) and 2,3,4,6-tetrachlorophenol (tetraCP). Furthermore, the potential utilization of less-pure ferrates was also studied as their lower price is an important factor for their practical use.

Materials and methods

Chemicals

Commercially available potassium ferrate (>90 % K_2FeO_4) obtained from Sigma-Aldrich (SA) was used in this study. Furthermore, two semi-pilot scale batches of ferrates (labelled as LAC A and LAC B) were manufactured and provided by the company LAC. The LAC A and LAC B ferrates were prepared under different conditions by high-temperature synthesis from iron oxide precursors and a nitrate oxidation agent according to patent no. US4545974. The content of Fe was determined by elemental analysis as being 26.4 % Fe (LAC A) and 22.3 % Fe (LAC B). Room temperature [57]Fe Mössbauer spectroscopy determined iron oxidation states as follows: 16 % Fe(V) and 84 % Fe(III) (LAC A), 45 % Fe(V) and 55 % Fe(III) (LAC B). Thus, the atomic mass ratio of Fe(V) was 4.2 % in LAC A and 10.0 % in LAC B (calculated from elemental analysis and Mössbauer spectroscopy).

Stock ferrate solutions were prepared by dissolving different weights (depending on ferrate purity and required final FeO_4^{2-} concentrations) of the solid sample in cooled

demineralized water (obtained using a PURELAB flex system [ELGA LabWater]). Due to the inhomogeneity of the ferrate material, it was not possible to calculate precise ratios in advance. Hence, final concentrations of the Fe(VI) stock solutions were calculated retrospectively after photometric measurement. For this reason, the ratios in the experiments varied slightly. All of the Fe(VI) stock solutions were used within 15 min of preparation. On average, after dissolution of 0.5 g of the "LAC A" in 1 l of distilled water, the solution contained 0.19 mM Fe(VI), and for "LAC B" 0.55 mM Fe(VI).

A saturated stock solution of PCP was prepared by dissolving standard PCP (purity 98.3 %; Supelco) in demineralized water. After three days of vigorous stirring, the solution was filtered through a 0.45 μm filter. The resulting concentration was 1.63 mg/l, which corresponded to 6.15 μM. The stock solution was then stored in a refrigerator at 5 °C.

Pentachlorophenol $^{13}C_6$ (purity 98 %; Sigma-Aldrich) was used as an internal standard (ISTD). The stock solution of ISTD was prepared by dissolving a solid standard in pure ethanol (Lachner) to the concentration of 7.6 mg/l.

Real contaminated groundwater from a former pesticide production site was obtained from Spolana Neratovice, Czech Republic. The complex contaminated water contained, among other pollutants, the following organic compounds: more than 2 mg/l sum of HCH (α, β, γ, δ and ε), 1.5 μg/l sum of DDD (dichlorodiphenyldichloroethane), DDE (dichlorodiphenyldichloroethylene) and DDT (dichlorodiphenyltrichloroethane), 30 mg/l sum of chlorobenzenes, 750 μg/l BTEX (benzene, toluene, ethylbenzene and xylenes), 20 μg/l sum of chloroethylenes and 107 μg/l sum of 6 chlorophenols (2-CP, 4-CP, diCP, triCP, tetraCP and PCP). pH of the Spolana water was 6.6, conductivity was 217 mS/m, alkalinity and acidity expressed by $ANC_{4.5}$ and $BNC_{8.3}$ were 3.33 mM and 2.55 mM, respectively, and COD-Cr was 52 mg/l.

Other chemicals used in the laboratory experiments were purchased as analytical grade and used without further purification. These included Na_2SO_3, NaOH and H_3BO_3 all from Lachner, acetic anhydride from Sigma-Aldrich, hexane for pesticide residue analysis from J.T. Baker and K_2CO_3 from Penta; the CPs (2-CP, 4-CP, diCP, triCP, tetraCP and PCP) were obtained from Sigma Aldrich, Supelco Analytical and Dr. Ehrenstorfer GmbH.

Methods

Experiments with spiked PCP water were performed in a reaction volume of 50 ml. Of H_3BO_3/NaOH buffer (pH 9) were placed into a reactor, spiked with 2 ml of PCP saturated stock solution and finally 5 ml of SA ferrate solution was added under vigorous stirring. The concentration of FeO_4^{2-} in the reactor was determined as 66.5 μM (i.e. 13.2 mg/l K_2FeO_4), and the concentration of PCP was 0.25 μM (which corresponded to 66.6 μg/l). After a specific time (i.e. 1, 3, 6,

9, 12, 15, 18, 21, 25 and 30 min), the reaction was stopped by an addition of 1 ml of 0.2 M Na_2SO_3 solution, which immediately reduced the ferrate. The experiments were performed in duplicate at ambient temperature.

Experiments with real contaminated groundwater were performed in the same reaction volume, i.e. 50 ml. Of groundwater buffered to pH 9 by H_3BO_3/NaOH, 40 ml was placed into a reactor and 10 ml of the appropriate ferrate solution was added. As there were other organic and inorganic constituents in the water, a higher concentration of FeO_4^{2-} in the reaction solution had to be used. Final concentrations of FeO_4^{2-} in the reactors varied slightly and were 290, 308 and 254 μM of SA, LAC A and LAC B ferrate, respectively. Furthermore, half FeO_4^{2-} concentrations were also used in the case of LAC A and LAC B ferrates. Experiments were performed in triplicate at ambient temperature and were left to react overnight. In addition to PCP, 2-CP, 4-CP, diCP, triCP and tetraCP were also monitored.

Prior to GC-MSMS analysis, acetylation and extraction of the products were performed according to ISO EN 12673. Of ISTD stock solution, 200 μl was added into each reaction flask. Extraction of the whole reactors (solution including the precipitation formed during the treatment) with 5 ml of hexane (shaking for 5 min at 150 rpm) followed the reaction with purified acetic anhydride. Each set of samples included controls, which were identically prepared as the samples but water was added instead of ferrate.

Analytical methods

CPs (acetylated derivatives) were determined in hexane extracts using a Trace 1310 gas chromatograph fitted with a triple quadruple tandem TSQ 8000 mass spectrometry detector (Thermo Scientific™). Fe(VI) concentrations were determined using a Lambda 35 UV/VIS absorption spectrometer (PerkinElmer Instruments) with molar absorptivity of 1150 M^{-1} cm^{-1} at 505 nm (Licht et al. 2001). Measurements of pH were carried out using a pH50 pH meter (Giorgio Bormac), which was calibrated using standard pH 4.01, 7.00 and 10.01 buffers.

Results and discussion

PCP reactivity with ferrate in spiked demineralized water

Water spiked with PCP was treated by ferrate to prove the hypothesized degradation of PCP in a PCP/Fe(VI) system. The reaction was carried out at pH 9 in order to keep the optimal stability conditions of ferrate (Li et al. 2005). The oxidation was stopped after specific times to watch the gradually decreasing concentration of the target compound. Figure 1 shows the decline of PCP over time. It is clear that

Fig. 1 Time-dependent concentrations of PCP in the presence of 66.5 μM SA FeO_4^{2-} in spiked water system at pH 9 (mean+standard deviation; μM)
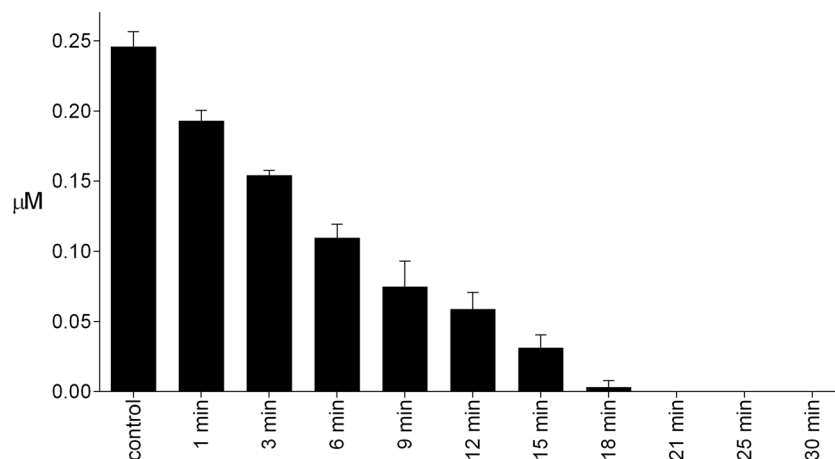
the ferrate degraded the PCP; moreover, the degradation was total. Under our experimental conditions, there was less than 1 % of initial PCP left after 21 min (Fig. 1).

PCP reactivity with ferrate in real groundwater

Considering the effective degradation of PCP by ferrate in a spiked water system, this degradation (along with the degradation of other CPs) was also studied under real conditions, namely in complex contaminated water from a former production facility. As the groundwater contained other organic and inorganic constituents, a higher concentration of ferrate (i.e. 290 μM of SA ferrate) was necessary to be used. The results shown in Table 1 indicated a total degradation of 2-CP, 4-CP, diCP, triCP and tetraCP. The vast majority of PCP was degraded too. Its residual concentration was 0.2 μg/l, which corresponded to less than 1.4 % of its initial amount.

Less pure ferrates

In order to study the effectiveness of PCP degradation by less pure ferrates, two batches of semi-pilot ferrates LAC A and LAC B (for the Fe(V) content see the 'Chemicals' section) were used. The weight of the added ferrates was set to values so that the FeO_4^{2-} concentrations in the reactors corresponded to the values in the experiments with SA ferrate. In addition, half concentrations of ferrates (LAC A-2 and LAC B-2) were used in order to study the effect of the dose on the degradation range.

Figure 2 provides an overview of CP degradation, while the individual values can be found in Table 2.

It is apparent from this data that both monochlorophenols as well as diCP were totally degraded by each of the ferrates in both concentrations. Furthermore, triCP and tetraCP were completely degraded by LAC B ferrate at both its concentrations. Regarding PCP, the vast majority was degraded by LAC B, specifically 99 % with the original dose and 92 % with the half dose. (The irregularity in the decrease of PCP after dosing with the whole or the half dose compared to the expected 50 % decline was caused by the fact that 1 % of the initial amount was the actual detection limit.) Comparing these results with the results shown in Table 1, it can be seen that the same range of CP degradation was achieved by both LAC B and SA ferrate in the approximate concentration of 280 μM FeO_4^{2-}. The results obtained by the treatment of less pure ferrate, LAC A, were in a good agreement with an already described trend (Olaniran and Igbinosa 2011) of increasing stability and thus persistence with increasing chlorination of the compound. Furthermore, as expected, the degradation of CPs was lower when the half doses were applied.

Despite the similar final concentration of FeO_4^{2-} in the reactor originating either from LAC A or LAC B ferrate, there was a significant difference in its efficiency for CP/PCP removal (Fig. 2). We believe that this can be explained by the different amounts of individual iron species originally present. Fe(V) (instantly forming FeO_4^{2-} and Fe(III) in water) is the species causing the degradation of PCP. On the other hand, Fe(III) is the ballast form producing Fe(III) colloids, which

Table 1 Concentrations of CPs in real groundwater after 24 h in the presence of 290 μM SA FeO_4^{2-} (mean±standard deviation; μg/l)

	Concentration (μg/l)					
	2-CP	4-CP	diCP	triCP	tetraCP	PCP
Control	11.13±0.88	31.85±1.68	3.35±0.09	2.86±0.13	13.13±0.33	14.86±0.17
Treated samples (290 μM SA ferrate)	<0.15	<0.15	<0.15	<0.15	<0.15	0.20±0.02
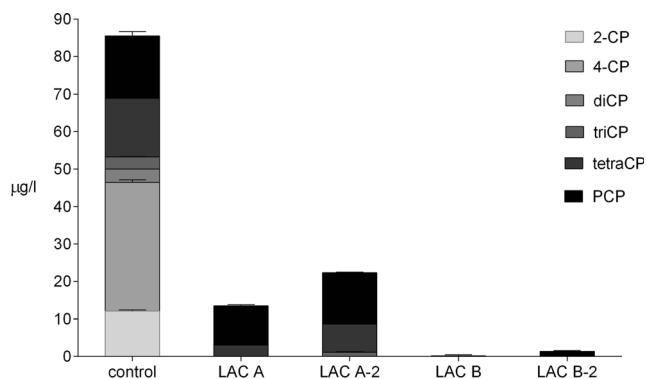
Fig. 2 Concentration of CPs in real groundwater after 24 h in the presence of approximately 290 μM LAC A or LAC B ferrates; LAC A-2 and LAC B-2 are half ferrate concentrations (mean+standard deviation; μg/l)

accelerate the spontaneous decay of the ferrate(VI) in the solution by heterogeneous catalytic reaction (Jiang and Lloyd 2002; Jiang et al. 2015; Goodwill et al. 2015). In order to maintain the same FeO_4^{2-} concentration in the reactors, a three times bigger dose of LAC A had to be used (LAC A contained approximately three times less Fe(V) than LAC B—see the 'Chemicals' section). Because of this, the concentration of Fe(III) in the LAC A solution was almost five times higher than that in the LAC B solution (see the 'Chemicals' section). This contributed to an inefficient decomposition of FeO_4^{2-} and thus to a lower efficiency of LAC A ferrate. A more detailed investigation of the influence of the Fe(III) dosage would be needed; nevertheless, according to our results, even almost 50 % of iron in the form of Fe(III) did not prevent the FeO_4^{2-} from almost totally degrading the pollutants (Jiang and Lloyd 2002). As the ratio of Fe(III)/Fe(V) increased, the efficiency of the degradation dropped.

We conclude that a degradation of pollutants by cheaper, more widely available but less-pure ferrates is possible (they may be applicable for remediation), albeit they are less efficient due to their higher Fe(III)/Fe(V) ratios. On the other hand, the cost of the subsequent sludge management has to be considered.

Table 2 Concentrations of CPs in real groundwater after 24 h in the presence of 290 μM LAC A or LAC B ferrates; LAC A-2 and LAC B-2 are half ferrate concentrations

	% of the initial amount					
	2-CP	4-CP	diCP	triCP	tetraCP	PCP
Control	100	100	100	100	100	100
LAC A	<1	<1	<1	<1	20	63
LAC A-2	<1	<1	<1	36	48	82
LAC B	<1	<1	<1	<1	<1	1
LAC B-2	<1	<1	<1	<1	<1	8

Conclusions

The present paper is the first to study the applicability of FeO_4^{2-} for PCP degradation/removal in water. The results proved that ferrate could be suitable for such an application, as all of the CPs, including the most persistent PCP, were completely removed. Total degradation did indeed take place; the removal was not caused by sorption on the iron precipitation as the whole content of the reactors was extracted into hexane. This degradation was confirmed both in the spiked water system as well as in real complex contaminated water from a former pesticide production area. Furthermore, utilization of less pure ferrates was also discussed. Further work needs to be done to establish the kinetic constants of CP degradation by ferrate. The degradation products along with the degradation pathway also remain to be found.

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A study of the reaction of ferrate with pentachlorophenol – kinetics and degradation products

M. Homolková, P. Hrabák, N. Graham and M. Černík

ABSTRACT

Pentachlorophenol (PCP) is a persistent pollutant which has been widely used as a pesticide and a wood preservative. As PCP is toxic and is present in significant quantities in the environment, there is considerable interest in elimination of PCP from waters. One of the promising methods is the application of ferrate. Ferrate is an oxidant and coagulant. It can be applied as a multi-purpose chemical for water and wastewater treatment as it degrades a wide range of environmental pollutants. Moreover, ferrate is considered a green oxidant and disinfectant. This study focuses on the kinetics of PCP degradation by ferrate under different pH conditions. The formation of degradation products is also considered. The second-order rate constants of the PCP reaction with ferrate increased from 23 $M^{-1}\,s^{-1}$ to 4,948 $M^{-1}\,s^{-1}$ with a decrease in pH from 9 to 6. At neutral pH the degradation was fast, indicating that ferrate could be used for rapid removal of PCP. The total degradation of PCP was confirmed by comparing the initial PCP molarity with the molarity of chloride ions released. We conclude no harmful products are formed during ferrate treatment as all PCP chlorine was released as chloride. Specifically, no polychlorinated dibenzo-*p*-dioxins and dibenzofurans were detected.

Key words | degradation product, ferrate, oxidation, pentachlorophenol, persistent organic pollutant (POP), reaction kinetics

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INTRODUCTION

Persistent organic pollutants (POPs) are compounds listed in the Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention on Persistent Organic Pollutants) which was incorporated into EU legislation in 2004 (Regulation (EC) No. 850/2004). Their basic characteristic is that these toxic organic compounds are resistant to environmental degradation through chemical, biological and photolytic processes. Thus, they become widely dispersed and can bio-accumulate in the fatty tissue of living organisms. Pentachlorophenol (PCP) is one of the pesticides proposed for listing under this convention (Stockholm Convention on POPs).

PCP has been widely used as an insecticide, a pesticide and a wood preservative for many decades (Exon 1984). Nowadays, the application of PCP and its related compounds is prohibited or restricted in the majority of countries. However, it is still produced (worldwide production estimated at ten thousand tonnes) or used in some countries as a wood preservative (Stockholm Convention

on POPs). There is a need to establish a suitable, effective and environmentally sustainable ('green') remediation process for this compound. According to the literature, photocatalysis (Piccinini *et al.* 1998; Hong *et al.* 2000), ozonation (Sung *et al.* 2012), hydrogen peroxide (Gupta *et al.* 2002) and persulphate are used for chemical oxidation of PCP to non-toxic compounds. Described products/intermediates are hydroxyl- and chloro-derivates of carboxylic acids, alcohols, phenols and quinones (Piccinini *et al.* 1998; Hong *et al.* 2000; Gupta *et al.* 2002; Qi *et al.* 2015). Furthermore, the formation of dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) (Hong *et al.* 2000; Czaplicka 2014) has also been reported. One potential but not yet described remediation process is the utilization of a high oxidation state of iron, ferrate (hexavalent iron FeO_4^{2-}). As far as is known, its principal decomposition product in redox reactions is non-toxic ferric ion, and no problematic by-products are created during treatment (Tiwari & Lee 2011). Therefore, ferrate may be used in the field of

environmentally sustainable water treatment not only as an oxidant and/or a disinfectant but also as a coagulant or sorbent (Filip *et al.* 2011). Of principal importance is that ferrate exhibits high reactivity, high oxidation reduction potential (ORP) and thus the ability to degrade various water pollutants (Sharma 2002; Tiwari & Lee 2011).

The reactivity and ORP of ferrate together with its stability depend strongly on pH. Under acidic conditions, an Fe(VI) solution reacts very rapidly with water and/or pollutants, while a high rate of self-decomposition takes place. At neutral or slightly alkaline conditions, the solution reacts slowly, and the lowest reaction rate occurs at pH 9–10. The rate increases slightly at a higher pH due to the formation of anionic species (Lee & Gai 1993; Lee *et al.* 2004; Li *et al.* 2005). The increasing reactivity/self-decomposition of ferrate with decreasing pH can be explained by its speciation. Fe(VI) exists in four different protonation states depending on pH: $H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$ and FeO_4^{2-} with pKa of 1.6, 3.5 and 7.3, respectively (Figure 1) (Carr *et al.* 1985; Rush *et al.* 1996; Sharma 2002; Li *et al.* 2005). A more protonated species is less stable and therefore more reactive (Rush *et al.* 1996). This corresponds to the redox potential, which is very different for acidic and basic conditions. Under basic conditions it is only +0.72 V, while under acidic conditions it is +2.20 V (Wood 1958), which is higher than any other oxidant/disinfectant used in water and wastewater treatment (Jiang & Lloyd 2002; Lee *et al.* 2004).

There have been many previous studies concerning the degradation of various organic pollutants by ferrate in water (Tiwari & Lee 2011; Jiang 2014). The first study on the degradation of PCP and other chlorophenols by ferrate in both spiked and real contaminated groundwater was recently published (Homolkova *et al.* 2016), but no detailed investigation explaining redox processes, their kinetics and
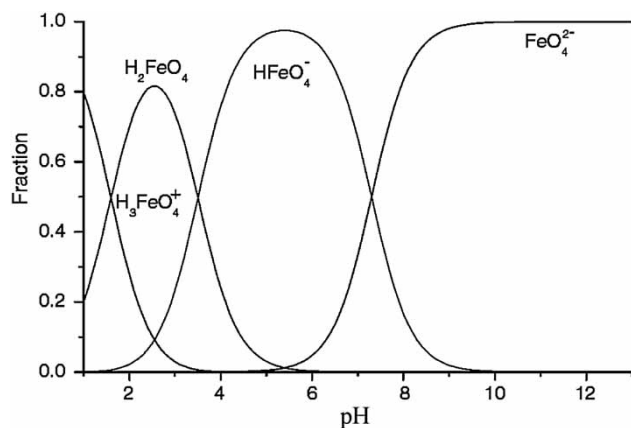
pH dependence has been published so far. The present study considers the kinetics of the reaction between ferrate and PCP under different pH conditions in the range of 6 to 9 at ambient temperature. In addition, the potential formation of degradation products was studied to confirm that no toxic compounds are produced during this treatment.

METHODS

Chemicals

Potassium ferrate ($>90\%$ K_2FeO_4) was obtained for the kinetic study from Zhenpin Chemical Engineering Ltd. (Shanghai, China) and for the study of degradation products from Sigma-Aldrich. Ferrate stock solutions were prepared by dissolving K_2FeO_4 powder in demineralized water just prior to each experiment and were stable during the period of use. Due to the non-homogeneity of the ferrate material and the handling of very small quantities, the final concentrations of the Fe(VI) stock solutions varied slightly ($\pm 5\%$) with the average concentration being around 100 µM FeO_4^{2-} for the kinetic experiments and 500 µM FeO_4^{2-} for the degradation-products experiments.

Stock solutions of PCP were prepared by dissolving standard PCP (purity 98%; Aldrich) in demineralized water and filtering through a 0.45 µm membrane, after vigorous stirring and ultrasound treatment, resulting in a concentration of 13 µM for the kinetic experiments and a concentration of 54 µM for the degradation-products experiment. The stock solutions were then stored in the dark at 5 °C.

Ammonium bicarbonate buffer (10 mM) was prepared from NH_4HCO_3 (Fluka analytical) and adjusted to the required pH (6, 7, 7.5, 8, 8.5 or 9) by 1 M HCl or 0.1 M NH_3. The stock solution of 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) and the 0.6 M acetate/0.2 M phosphate buffer were prepared as described elsewhere (Lee *et al.* 2005a). High-performance liquid chromatography (HPLC) grade acetonitrile, water and formic acid (98%) were supplied from Sigma Aldrich. Calibration solutions of PCP were prepared in acetonitrile and stored in the dark at 5 °C.

Methods

Kinetic experiments

The reaction rates of PCP oxidation by Fe(VI) were determined with an excess of ferrate. The initial molar ratio of Fe(VI):PCP was 30:1. The experiments were performed in a

Figure 1 │ Relative amounts of Fe(VI) species under various pH conditions (Carr *et al.* 1985; Rush *et al.* 1996; Sharma 2002; Li *et al.* 2005).

reaction volume of 100 mL, where 50 mL of ammonium bicarbonate buffer of the appropriate pH was spiked with 10 mL of PCP stock solution and finally 40 mL of ferrate stock solution was added. The experiment at pH 6 was conducted using half concentrations (5 mL of PCP and 20 mL of ferrate stock solution in 75 mL of buffer) as the kinetics at such a pH were very rapid. In all of the kinetic experiments, 5 mL of the reaction solution was periodically withdrawn from the reactor and placed into a vial containing 5 mL of acetate/phosphate buffer and 1 mL of ABTS stock solution, which quenched the oxidation reaction almost immediately by the rapid reaction of ABTS and Fe(VI) ($k = 1.2 \times 10^6$ M^{-1} s^{-1} at pH 7) and formed a green coloured radical ABTS$^{•+}$ solution (Lee *et al.* 2005a). Finally, 14 mL of water was added. The resulting green coloured samples were divided into two parts. The first part was used to determine the PCP concentration using liquid chromatography after filtration through a 0.2 μm membrane, and with the second part the FeO_4^{2-} concentration was determined photometrically. The blank experiments were provided at the same pH but without Fe(VI); instead, water was added. This was done to capture any potential spontaneous PCP decrease and to measure the precise amount of PCP dosed.

Analysis of degradation products

Degradation products were studied through the comparison of chloride release during the reaction and through the determination of evolved PCDD/F (polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans) and PCB (polychlorinated biphenyls) during the reaction. The experiments concerning the total degradation of PCP were performed in a very simple system. The ferrate stock solution was directly added into water containing PCP without any pH adjustment. The applied doses of the individual chemicals are summarized in Table 1. This resulted in the approximate concentration of 27 μM and 250 μM of PCP and Fe(VI), respectively. Each sample was prepared in quadruplicate.

Table 1 | Dosed amounts for the analysis of degradation products

	Demineralized water	PCP stock solution (54 μM)	Fe(VI) stock solution (500 μM)
Blank water	40 mL	–	–
Blank ferrate	20 mL	–	20 mL
Base PCP	20 mL	20 mL	–
Reaction samples	–	20 mL	20 mL

Blanks and base samples were prepared in order to evaluate the potential amounts of chloride present in the chemicals employed. The precise amount of dosed moles of PCP was confirmed from the base samples. Chloride ions were determined after filtration through a 0.22 μm membrane using an ion chromatograph (details in the following section).

The samples for the analysis of PCDD/F and PCB were prepared in the same way, as shown in Table 1. This was done in duplicate.

Analytical methods

Fe(VI) concentrations were determined using a UV-VIS spectrophotometer (UV-2401 PC, Shimadzu) based on a molar absorptivity of the green coloured radical ABTS$^{•+}$ of 34,000 $M^{-1} \cdot cm^{-1}$ at 415 nm (Lee *et al.* 2005b) in the case of the kinetic experiments. The Fe(VI) concentration for the chloride release experiment was determined using a Lambda 35 UV/VIS absorption spectrometer (PerkinElmer Instruments) with a molar absorptivity of 1,150 $M^{-1} \cdot cm^{-1}$ at 505 nm (Bielski & Thomas 1987).

The concentration of PCP was determined using a Waters Acquity ultra performance liquid chromatography (UPLC) system (Waters Corp.) with a high definition mass spectrometer (Waters Synapt G2-Si). The mobile phases were water (MF A) and acetonitrile (MF B), both adjusted to pH < 2.5 by formic acid, at a constant flow of 0.5 ml/min. The MF B was increased from 20% to 100% in 5 min, held for 2 min, and then returned to the initial conditions (20% B) in 0.01 min. Such conditions were maintained for 8 min. The retention time of PCP was 3.9 min, using an Acquity UPLC HSS C18 1.8 μm, 2.1 × 100 mm column (Waters Corp.).

An ion chromatograph (ICS 2100, Thermo) with suppressed conductivity detection was employed for the chloride measurements. This was equipped with an Ion Pack AS19 250/2 column with 8 mM KOH electrolytically generated eluent.

Quality control samples and system blanks were measured at the beginning and at the end of each sequence and after each ten samples. Calibration was measured with eat set of samples.

The concentration of PCDD/F and PCB was determined by a commercial laboratory (Axys-Varilab, Czech Republic) using gas chromatography/high-resolution mass spectrometry (GC-HRMS) (Autospec Ultima) according to CSN EN 1948-2,3. The determination consists of extraction procedures, extract cleaning procedures and GC injection followed by HRMS detection of exact masses specific for selected PCDD/F + PCB congeners. During the analysis, isotopically

labelled congeners are added to follow the recovery and other parameters specified in the isotopic dilution method.

RESULTS AND DISCUSSION

Kinetic experiments

The rate equation for PCP oxidation by Fe(VI) can be expressed by Equation (1), where [PCP] and [Fe(VI)] are the concentrations of PCP and Fe(VI), respectively, and k is the second-order reaction rate constant. Under the pH conditions tested (pH $\geq$ 6) it can be assumed that PCP was present in the fully dissociated form (pKa $\sim$ 4.7).

$$-d\frac{[PCP]}{dt} = k[PCP][Fe(VI)] \qquad (1)$$

The decrease of PCP and Fe(VI) concentrations was measured to determine the rate constant of PCP oxidation by ferrate. The second-order rate constant k was determined under pseudo first-order reaction conditions. Under such conditions, one reactant is used in a large excess, and thus its concentration is considered to be constant over the entire reaction time. Therefore, the k value can be calculated from the integration of Equation (1) as shown in Equation (2):

$$ln\frac{[PCP]}{[PCP_0]} = -k[Fe(VI)]\int_0^t dt \qquad (2)$$

However, this equation cannot be used, as Fe(VI) is unstable in aqueous solution and decomposes to Fe(III) (Machala *et al.* 2009). In such a case (where the concentration of the reactants cannot be considered stable), the k

value can be determined at a given pH by the integration of Equation (1) as follows:

$$ln\frac{[PCP]}{[PCP_0]} = -k\int_0^t [Fe(VI)]dt \qquad (3)$$

and graphically from the slope of the log of PCP removal as a function of time integrated Fe(VI) concentration. Such a method has already been used in other studies, e.g. for the determination of kinetics of the reaction of ferrate with bisphenol A (Lee & Yoon 2004) and with phenolic endocrine disrupting chemicals (Lee *et al.* 2005a).

Figure 2(a) and 2(b) show the kinetic data of Fe(VI) and PCP decomposition under different pH conditions, respectively. According to the literature mentioned above, Fe(VI) decomposition is a complicated, strongly pH-dependent process. Our results showed almost negligible decomposition at pH 8.5 and 9.0 (Figure 2(a)) during a period of 10 min, which is in agreement with results described previously (Lee & Gai 1993; Lee *et al.* 2004; Li *et al.* 2005). The results also show that the decrease in the Fe(VI) concentration caused by its reaction with PCP was negligible, as ferrate was in a significant excess. At lower pH, the concentration of ferrate decreased during the reaction. This was caused by the self-decay of ferrate/reaction with water (Lee & Gai 1993; Rush *et al.* 1996; Jiang & Lloyd 2002):

$$Fe^{VI}O_4^{2-} + (5/2)H_2O \rightarrow Fe^{III}(OH)_3 + 2(OH^-) + (3/4)O_2 \uparrow$$
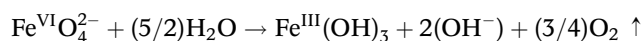
The lower the pH, the more rapid the decrease in Fe(VI) was observed, which can be explained by an increasing presence of more protonated species (Figure 1). The ferrate decomposition was also supported by a relatively high ferrate concentration and temperature, as the experiments
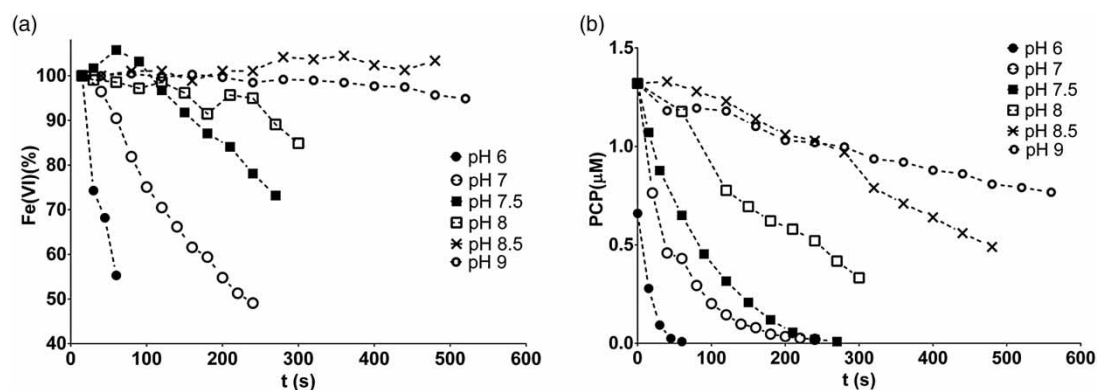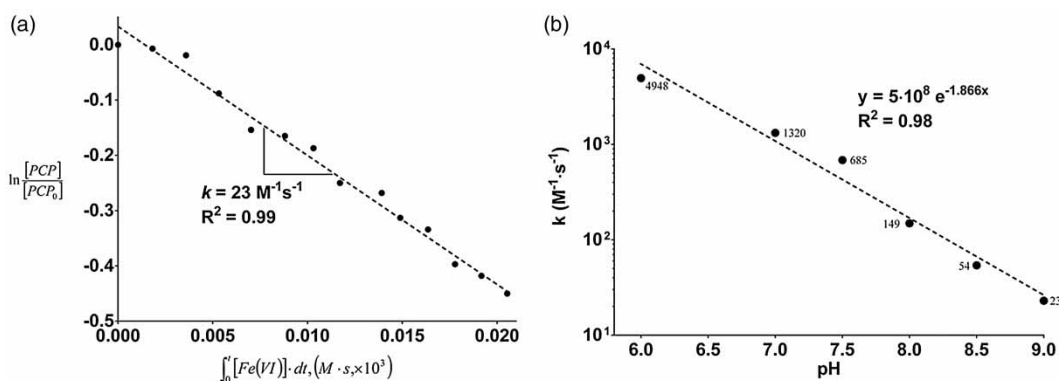

Figure 2 | Time profile of Fe(VI) (a) and PCP (b) concentrations under different pH conditions.

Figure 3 | (a) An example of a graphical expression of Equation (2) for pH 9; (b) the dependency of rate constant k on pH.

were conducted under ambient conditions (Jiang & Lloyd 2002; Li *et al.* 2005).

PCP degradation (Figure 2(b)) was significant throughout the whole range of pH conditions studied. The blank experiments confirmed no spontaneous PCP decrease (data not shown). The efficiency of the degradation process at pH 8.5 and 9.0 was high, as an almost negligible decrease in Fe(VI) concentrations caused a significant decomposition of PCP. The faster PCP removal under more acidic conditions was expected, as ferrate is more reactive at lower pH. This is caused by the increasing concentration of the more protonated species (see Figure 1) and thus by the higher redox potential. According to Lee *et al.* (2005a), $HFeO_4^-$ was the species which reacted predominantly in the whole pH range studied (6–9) and thus contributed significantly to the overall reaction. This was assumed as the rate of the degradation decreased together with the decreasing $HFeO_4^-$ concentration with increasing pH. The contribution of FeO_4^{2-} to the overall reaction rate was negligible. At pH 7.5 or lower, the PCP completely degraded within 300 s (5 min). On the other hand, the efficiency of the process was lower due to increasing ferrate self-decay.

The second-order rate constants k of PCP degradations were obtained from Equation (2). The graphical interpretation of Equation (2) is shown for data determined at pH 9 in Figure 3(a). The variation of the rate constant, k, with pH is shown in Figure 3(b), as log (k) versus pH. It is clear that the rate constant is strongly dependent on the pH of the reaction. The dependency of log k on pH can be considered as linear with a slope of −1.866.

Analysis of degradation products

PCP is a potential precursor of some of the most notorious environmental contaminants known, polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) (Hong *et al.* 2000; Czaplicka 2014). To evaluate the extent of PCP degradation and the presence of potentially harmful chlorinated intermediates produced during Fe(VI) oxidation of PCP, the total amount of chloride anions released from PCP was determined in separate experiments. These experiments were designed to be as simple as possible, with no buffering and no other chemicals added.

In the case of total PCP degradation, five moles of chloride ion are evolved from one mole of PCP. Table 2 summarizes the initial concentrations (μM) of PCP and final concentrations of chloride anions. Blank experiments confirmed that no significant amounts of chloride ions were contained in the ferrate solution involved and 12.42 μM was present as an impurity in the base PCP solution. The initial amount of PCP was 26.54 μM and the theoretical concentration of chloride that could be released by total compound degradation was 132.7 μM. The measured concentration of chloride after the reaction with Fe(VI) was 143.02 μM. After subtraction of the chloride impurity in the base PCP solution, the amount of chloride formed through Fe(VI) reaction was calculated as 130.61 μM, which corresponds closely to the initial chlorine content of PCP, within the experimental error (about 10%). Thus, it is clear that the vast majority of the PCP was fully degraded under our reaction conditions.

Table 2 | Resulting PCP and chloride concentration (mean ± standard deviation)

	PCP (μM)	Cl⁻ (μM)
Blank water	$<10^{-5}$	<5.6
Blank ferrate	$<10^{-5}$	<5.6
Base PCP	26.54 ± 3.12	12.42 ± 1.13
Reaction samples	$(26.7 \pm 14.6) \times 10^{-4}$	143.02 ± 3.39

As PCDD/F and dioxin-like PCB are harmful at very small concentrations, and as the experimental error in the above-mentioned experiment was about 10%, a separate analysis was performed to search for any PCDD/F and PCB that was produced by the reaction. Seventeen PCDD/F congeners and 18 indicator and dioxin-like PCB congeners were analysed. No significant increase in concentrations was found compared with the base samples (data not shown). Thus, we conclude that during the reaction of PCP and ferrate no harmful chlorinated compounds were produced.

CONCLUSIONS

In this paper the kinetics of PCP degradation by ferrate(VI) in water were investigated. Second-order reaction rates were determined under different pH conditions from pH 6 to pH 9. The rate constant decreased logarithmically with pH according to the following empirical relationship: k $(M^{-1} s^{-1}) = 5 \times 10^8 \exp(-1.866 \, pH)$. At lower pH values the reaction was significantly faster due to the greater oxidation potential of the protonated form of Fe(VI). As the degradation is sufficiently fast at neutral pH conditions ($k > 10^3 \, M^{-1} \, s^{-1}$), ferrate oxidation may be a suitable, effective and 'green' process for the treatment of water contaminated by this potentially harmful compound (PCP). The sustainability of this treatment was also confirmed by studying the degradation products of PCP. We confirmed the total degradation of PCP and the release of the associated chlorine as chloride anions under our reaction conditions. Furthermore, no detectible concentrations of PCDD/F and PCB were produced during the reaction, which was confirmed by GC-HRMS. Thus, no harmful products are formed from PCP during the reaction, and therefore we conclude that there are no potentially toxic effects during ferrate oxidation. The mechanism of PCP degradation by Fe(VI) is the subject of further research.

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CHEMICAL DEGRADATION OF PCDD/F
IN CONTAMINATED SEDIMENT

CHEMICZNA DEGRADACJA PCCD/F
W ZANIECZYSZCZONYM SEDYMENCIE

Abstract: Due to the extreme toxicity of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F), the remediation of PCDD/F aquifer source zones is greatly needed; however, it is very difficult due to their persistence and recalcitrance. The potential degradability of PCDD/F bound to a real matrix was studied in five systems: iron in a high oxidation state (ferrate), zero-valent iron nanoparticles (nZVI), palladium nanopowder (Pd), a combination of nZVI and Pd, and persulfate (PSF). The results were expressed by comparing the total toxicity of treated and untreated samples. This was done by weighting the concentrations of congeners (determined using a standardized GC/HRMS technique) by their defined toxicity equivalent factors (TEF). The results indicated that only PSF was able to significantly degrade PCDD/F. Toxicity in the system decreased by 65% after PSF treatment. Thus, we conclude that PSF may be a potential solution for in-situ remediation of soil and groundwater at PCDD/F contaminated sites.

Keywords: PCDD/F, ferrate, nZVI, Pd, persulfate, degradation

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are without doubt the highest priority groups of pollutants. They belong to the first groups of pollutants (called the Dirty Dozen) to be inscribed under the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2001. The aim of this convention is to protect human health and the environment from harmful and widely distributed chemicals by requiring its parties to eliminate or reduce the release of POPs into the environment [1].

Contrary to all other POPs, PCDD/F were never intentionally produced as organochlorinated pesticides as they are exclusively impurities/by-products with a varying origin. PCDD/F are highly toxic for human health and wildlife, remain intact in the environment for long periods of time, are widely distributed throughout the environment, and bioaccumulate in fatty tissues of humans and animals. Their toxic effect is mediated

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through the interaction with an intracellular protein, the aryl hydrocarbon receptor (AHR) [2], which occurs in most vertebrate tissues and affects a number of other regulatory proteins. The toxicity of PCDD/F depends on the number and position of the chlorine atoms in their molecule. Congeners with chlorines in the 2, 3, 7, and 8 positions have the highest affinity to the AH receptor and are therefore significantly harmful. Seven dioxins and ten furans have chlorines in these relevant positions and are considered toxic by the WHO-TEQ scheme (World Health Organization Toxic Equivalent) [2]. The most toxic dioxin is reported to be 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), which is the strongest known human carcinogen according to the International Agency for Research on Cancer [3]. On the contrary, PCDD/F containing between one and three chlorine atoms are not considered to be toxicologically serious, whereas other organic molecules, for example coplanar PCB or polychlorinated naphthalenes, possess dioxin-like toxicity [4, 5].

The WHO-TEQ scheme was adopted internationally as the most appropriate way of estimating the potential health risks of mixtures of PCDD/F as there are 75 PCDD and 135 PCDF possible congeners. The total TEQ value expresses the total sample toxicity as if only TCDD congener would be present. Each of the seven dioxin and ten furan toxic congeners is given a toxicity ranking called the toxic equivalency factor (TEF) from 0 to 1, where the reference congener is TCDD which by definition has a TEF = 1. Their concentration is then weighted by their TEF, which gives a congener contribution to the sample TEQ. Alternatively to calculating the specific congener contributions after GC/HRMS determination, a screening method based on cell-line with sensitized AHR could be used [4].

The remediation of PCDD/F contaminated soil is generally very difficult. Post-excavation soil cleaning methods mostly employ physical or chemical methods like thermal treatment [6, 7], surfactant washing [8, 9] or base-catalysed decomposition [10] of PCDD/F.

In this paper, we studied the potential degradation of PCDD/F bound to a real soil matrix by applying five different oxidants and reductants with a potential for in-situ remediation. Two extreme oxidation states of iron were tested: Fe^0 nanoparticles (zero-valent iron nanoparticles, nZVI) and Fe^{+6} (ferrate, Fe(VI)). Ferrate is a very strong oxidant whose superior performance for environmental remediation has been demonstrated in various recent researches [11-13]. On the other hand, ZVI in the form of nanoparticles is a strong reductant with a large specific surface and has been utilized for groundwater remediation and wastewater treatment [14, 15]. The second metal having a potential dechlorination capability was the catalytic, noble metal palladium in the form of a nanopowder. A combination of Pd and nZVI was also studied as it has been reported that such a combination improves the degradation rates of chlorinated compounds [16, 17] including PCDD/F [18, 19]. Finally, heat-activated PSF was tested as sulfate and hydroxyl radical generator. $SO_4^{\bullet-}$ and $OH^\bullet$ are one of the strongest known oxidants used for in situ chemical oxidation in the remediation of soil and groundwater [20].

Materials and methods

Chemicals

PCDD/F was used in the form of an industrial sandy soil certified reference material (BCR 529) [21] obtained from Sigma Aldrich. Information on the presence of the certified concentrations of PCDD/F is given in Table 1. The certified values were not available for

all of the congeners presented in the material; however, the concentrations of the other congeners were determined through analysis and were in good agreement with the data obtained by Antunes et al [22]. The toxicity equivalent factors (TEF) [23] used for dioxins are also given in Table 1.

Table 1

Composition of the certified reference material [21] and the TEF values [23]

PCDD/F (#)	Certified value [µg/kg]	Uncertainty [µg/kg]	TEF
2,3,7,8-TCDD (D1)	4.5	0.6	1
1,2,3,7,8-PeCDD (D2)	0.44	0.05	0.5
1,2,3,4,7,8-HxCDD (D3)	1.22	0.21	0.1
1,2,3,6,7,8-HxCDD (D4)	5.4	0.9	0.1
1,2,3,7,8,9-HxCDD (D5)	3.0	0.4	0.1
1,2,3,4,6,7,8-HpCDD (D6)	-	-	0.01
OCDD (D7)	-	-	0.001
2,3,7,8-TCDF (F1)	0.078	0.013	0.1
1,2,3,7,8-PeCDF (F2)	0.145	0.028	0.05
2,3,4,7,8-PeCDF (F3)	0.36	0.07	0.5
1,2,3,4,7,8-HxCDF (F4)	3.4	0.5	0.1
1,2,3,6,7,8-HxCDF (F5)	1.09	0.15	0.1
2,3,4,6,7,8-HxCDF (F6)	0.37	0.05	0.1
1,2,3,7,8,9-HxCDF (F7)	0.022	0.010	0.1
1,2,3,4,6,7,8-HpCDF (F8)	-	-	0.01
1,2,3,4,7,8,9-HpCDF (F9)	-	-	0.01
OCDF (F10)	-	-	0.001

Potassium ferrate was provided by the company LAC. The content of Fe was determined by elemental analysis as being 25.5% Fe. Room temperature ^{57}Fe Mossbauer spectroscopy determined the iron oxidation states as follows: 5% Fe(V), 7% Fe(VI) and 88% of Fe(III). This implies that the ferrate powder contained 5.5% K_3FeO_4 and 6.5% K_2FeO_4.

Standard NANOFER 25P nZVI (NANO IRON, s.r.o., Olomouc, Czech Republic) was used in the form of a dry powder preserved in an inert nitrogen atmosphere. The particles were without surface modification and had an average size of 50 nm, average surface area of 20-25 m^2/g and a narrow size distribution of 20-100 nm. The content of iron was high, ranging between 80 and 90 wt. %. An aqueous suspension of Fe^0 was prepared from the powder at a ratio of 1:4 nZVI:water, which yielded a suspension with an nZVI content of 200 g Fe^0/dm^3.

Palladium nanopowder (< 25 nm) with purity 99.9% was obtained from Aldrich. Sodium persulfate (PSF) of p.a. quality was obtained from Penta.

Methods

A total of 1.0 g of the certified BCR-329 material was placed into each reactor containing 522.5 cm^3 of demineralized water and stirred vigorously for 30 minutes. After that, the appropriate reactant (Fe(VI), nZVI, Pd, Pd+nZVI and PSF) was added. The reaction times differed in accordance to the reactant used. The dosed amounts of the individual chemicals together with durations of reactions are summarized in Table 2. The reaction of PCDD/F with Fe(VI) and nZVI was performed in triplicate and the reaction with Pd, Pd+nZVI and PSF in duplicate. The base samples consisting of water and PCDD/F

only were repeated nine times in total with reaction times ranging from 3 to 60 days, thus covering all of the different reaction times used in this study. PSF was activated by heat, namely at 50°C, during the whole reaction time.

Table 2

Dosed amounts and the reaction times

	Reaction time*	Fe(VI)	nZVI	Pd	PSF
Base	3-60 days	-	-	-	-
Fe(VI)	3 days	1.0 g	-	-	-
nZVI	60 days	-	5.0 g	-	-
Pd	22 days	-	-	0.1 g	-
Pd+nZVI	22 days	-	5.0 g	0.1 g	-
PSF	7 days	-	-	-	10.0 g

*reaction times were chosen on the previous experience with reagents reactivity - no remaining reducing/oxidizing effect is supposed to persist in reactors at the end of the reaction time

Analytical methods

The samples were processed in a commercial laboratory (ALS) by the standard extraction and cleaning procedure for PCDD/F, including the addition of the appropriate $^{13}C_{12}$ labelled internal standards according to EN 1948-2 [24]. The separation, identification and determination of PCDD/F in the extracts containing the standards for determining the recoveries were performed using GC/HRMS according to EN 1948-3 [25]. The seventeen congeners listed in Table 1 were determined.

Results and discussion

For clarity and simplification, all of the results were expressed as toxicity equivalency values (TEQ), which is a summary parameter evaluating the congener concentration weighted by its TEF.

The composition of the base samples was determined and the results were expressed as TEQ of each PCDD/F congener in each base sample as shown in Figure 1. Furthermore, the TEQ contribution of each average PCDD/F congener to the overall toxicity of the average base sample is shown in Figure 2. The total TEQ of the average base was determined as 11.138 ng/g.

It is apparent from Figure 2 that almost two thirds (specifically 6.8 ng/g, which corresponds to 61.1%) of the overall TEQ resulted from the D1 congener. The other relatively high contributions (but significantly lower in comparison to D1) were 7.4% and 6.0% for D4 and D6, respectively. The lowest TEQ was exhibited by F1, F2 and F9.

PCDD/F samples were treated by iron in its two extreme oxidation states, Fe^0 (nZVI) and Fe^{+6} (Fe(VI), ferrate), by palladium nanopowder (Pd), by a combination of Pd with nZVI and by PSF. The overall results of this study are summarized in Figure 3 where the columns represent summary TEQ values of all of the congeners. With the exception of the PSF treated samples, no significant degradation of the sum of PCDD/F was observed for any of the reactants. A distinct decrease in the overall PCDD/F toxicity and thus overall PCDD/F content was caused solely by PSF. This decrease was from 11.1 to 3.9 ng/g, which corresponded to 65%.
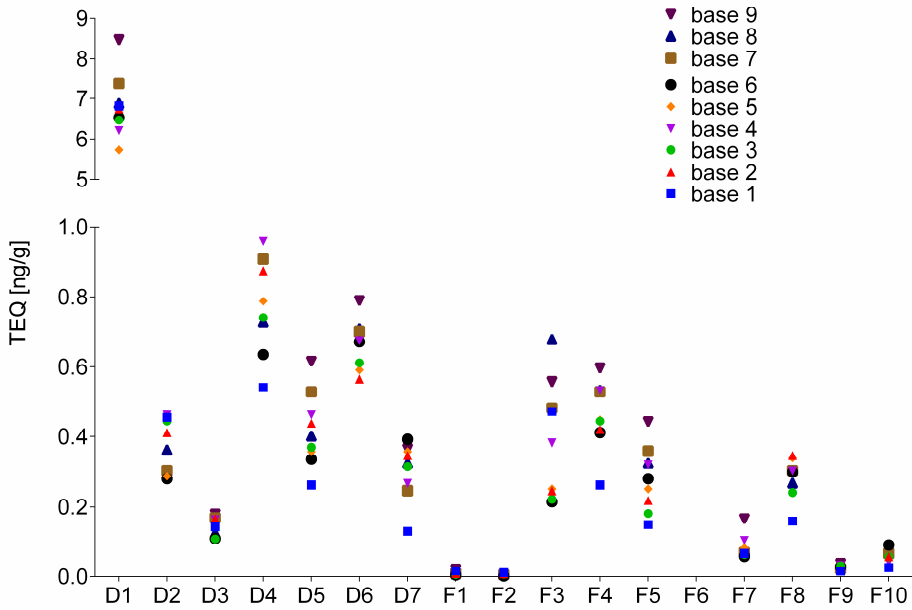
Fig. 1. TEQ of individual congeners in base samples
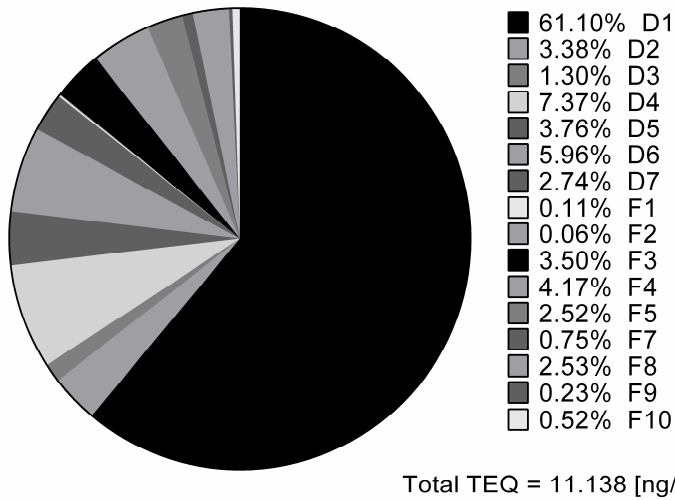

Fig. 2. Contribution of individual congeners to the overall toxicity of the base

Contrary to the PSF treated sample and to our presumption, the TEQ in ferrate treated samples increased. This could be explained by the ferrate oxidation of the real matrix containing PCDD/F, which could help/contribute to the release of PCDD/F bound to the matrix and thus a higher extraction yield could have been caused. However, the increase in

TEQ may also have been caused solely by experiment error, as the difference between the base and ferrate treated samples is within the range of standard deviation. The relatively high standard deviation ranges in the case of the ferrate and nZVI treated samples could be explained by difficult dosing of these two particular chemicals due to their inhomogeneity. In the case of ferrate, the inhomogeneity lies in the solid sample itself which was dosed; whereas nZVI was dosed in the form of an aqueous suspension, which is known to solve the problem of nZVI sedimentation and/or aggregation [26]. Neither nZVI (despite the highly reactive pyrophoric form used), nor Pd, nor even their combination, caused any significant degradation. As mentioned above, according to Kim et al [18], the combination of nZVI and Pd rapidly dechlorinates PCDD. However, in their study bimetallic palladized nanosized ZVI (Pd/nFe) was used. In contrast, only a simple mixture of nZVI and nanosized Pd was used in our experiment. This fact may explain our negative result, as such a contact between the two surfaces was not achieved in our study.
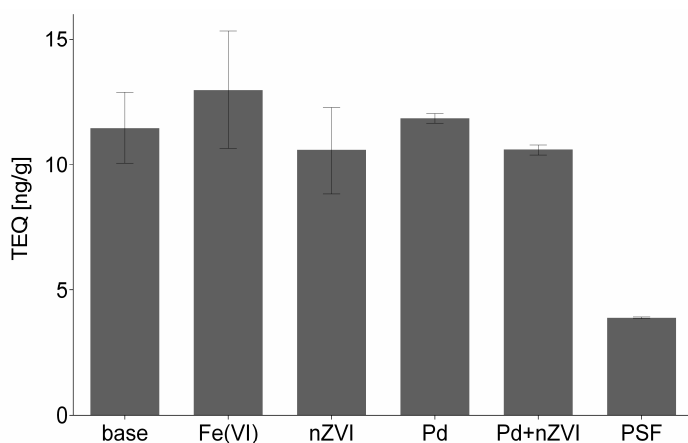

Fig. 3.   Summary of the whole study expressed in TEQ values (mean ± standard deviation)

The behavior of the individual congeners in the PSF treated samples and their contribution to the overall decline in TEQ are shown in Figure 4. The rate of decline differed for each PCDD/F congener; however, it is apparent that there was a decrease in each of them. No increase in the concentration of any of the congeners was observed. The most significant contribution to the overall decrease was exhibited by congeners D1, D2 and D4. When taking into account the relative values, the highest relative decline was observed for D2, F1 and F2, which decreased by 97.1, 91.4 and 85.3%, respectively; whereas the lowest observed decline was 28.5, 47.0 and 47.5% for F8, D6 and D7, respectively. One can conclude that high reactivity of PSF towards PCDD/F congeners can be due to the high reaction rate between both sulfate and hydroxyl radicals and the electron rich bonds in aromatic rings [27, 28].

As there was a different rate of decline of each PCDD/F congener after PSF treatment, their relative contribution to the overall toxicity of the sample changed (Fig. 5) compared to the base sample (Fig. 2). The highest contribution, more than one half, was still conclusively caused by D1, but the others did not lag so far behind this time. The highest

contributions to the total TEQ of PSF treated samples were 53.8, 9.5 and 9.0% for D1, D4 and D6, respectively.
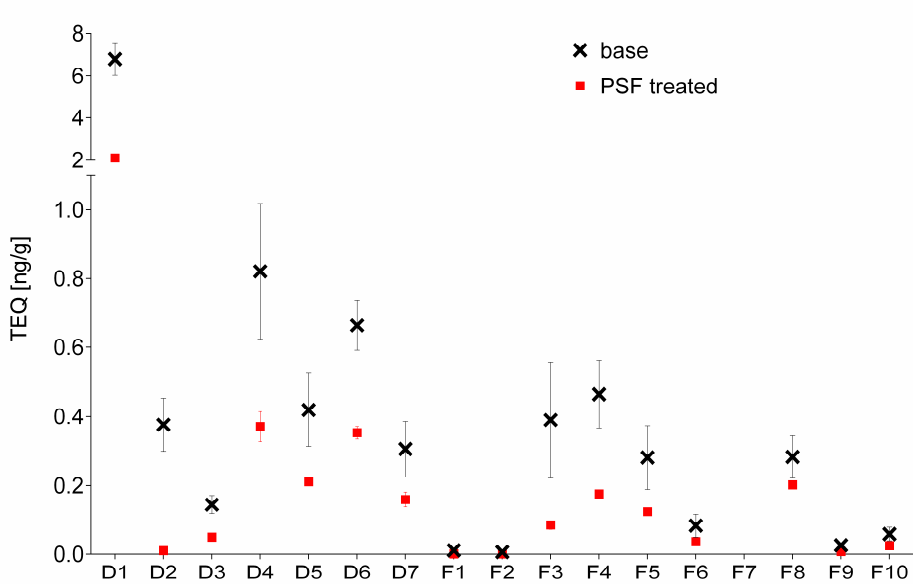

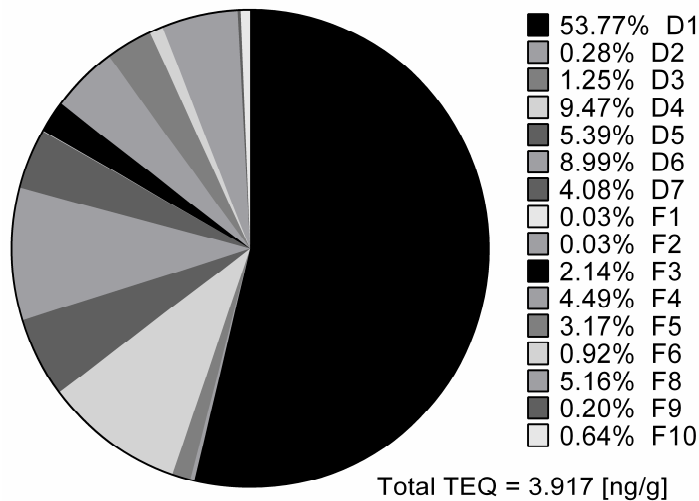Fig. 4. Decline of individual congeners in the PSF treated samples (mean ± standard deviation)

Fig. 5. Contribution of individual congeners to the overall toxicity of PSF treated samples

Only a few studies are comparable with our system. Kim et al [29] described approximately 15% TCDD degradation in a heat-activated persulfate system. In contrast to

the real soil matrix that we report here, Kim et al [29] dosed TCDD as being solvent-dissolved and started the reaction after complete acetone evaporation.

The behavior of individual congeners and their contribution to the overall PCDD/F TEQ increase in Fe(VI) treated samples is shown in Figure 6. It can be assumed that the overall behavior was caused mostly by D1 and partly by D4. Other congeners with increasing concentrations were D3, D5, D7, F2, F6 and F10. On the other hand, there are also congeners with decreasing concentrations. The highest relative decrease was observed in the case of F9 and F5 with 23.7 and 20.0%, respectively.
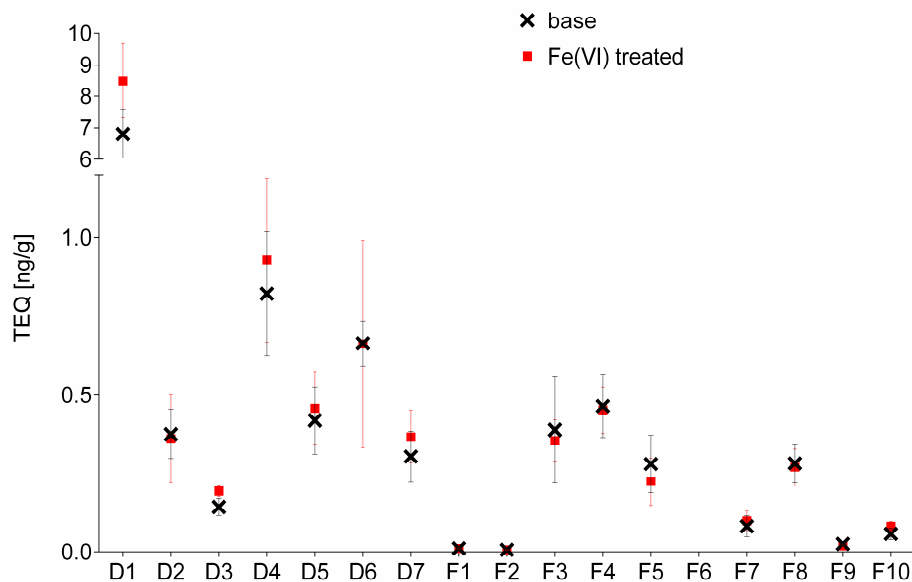

Fig. 6. Behavior of individual congeners in the Fe(VI) treated samples (mean ± standard deviation)

Conclusions

In this paper the potential degradation of PCDD/F bound to a real matrix was studied by five different oxidants and reductants commonly used for in-situ remediation, *ie* Fe(VI), nZVI, Pd, Pd+nZVI and PSF. We conclude that only the treatment by sulfate and hydroxyl radicals formed in the heat-activated PSF system exhibited a significant decrease in the PCDD/F concentrations. This decrease was 65% when comparing the total toxicity of the base and the treated samples. Thus, PSF activated at 50°C may be used for the remediation of aquifers contaminated by these priority pollutants. Future research should be devoted to studying wider range of activation temperatures, whereby the lower ones are of much technological interest. Other PSF activation procedures (electroactivation, alkaline activation or hydrogen peroxide activation as examples) have also a potential to create strongly mineralising conditions applicable for PCDD/F degradation.

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