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

VYUŽITÍ ŽELEZA VE VYSOKÉM OXIDAČNÍM STAVU PRO ČIŠTĚNÍ KONTAMINOVANÝCH VOD

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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 EDS, 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.

CONTENTS

1 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.

2 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.

My doctoral study resulted in four scientific papers on the degradation of various POPs by ferrates, which were published in impact journals. I am the first author in three of them and the corresponding author in the last one. Besides the abstracts of these papers presented in this presentation of the dissertation, a full paper on PCP is presented.

3 THEORETICAL PART

3.1 Ferrates

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).

3.1.1 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.

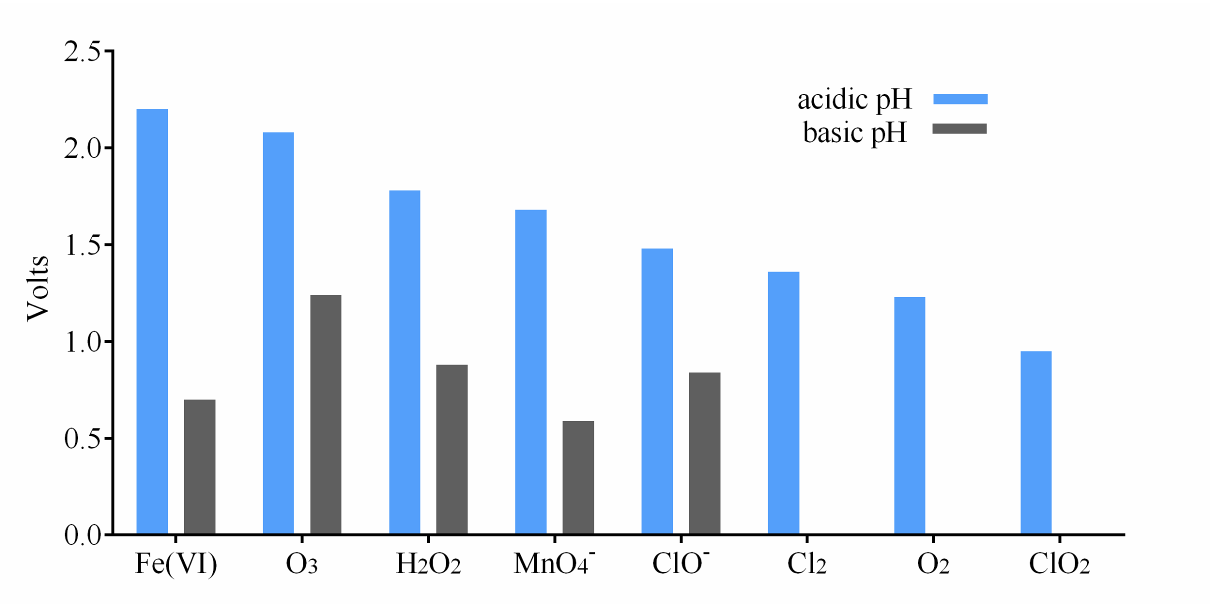

Figure 1: Redox potentials of ferrate and the oxidants/disinfectants used in WWT[32,40]

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.

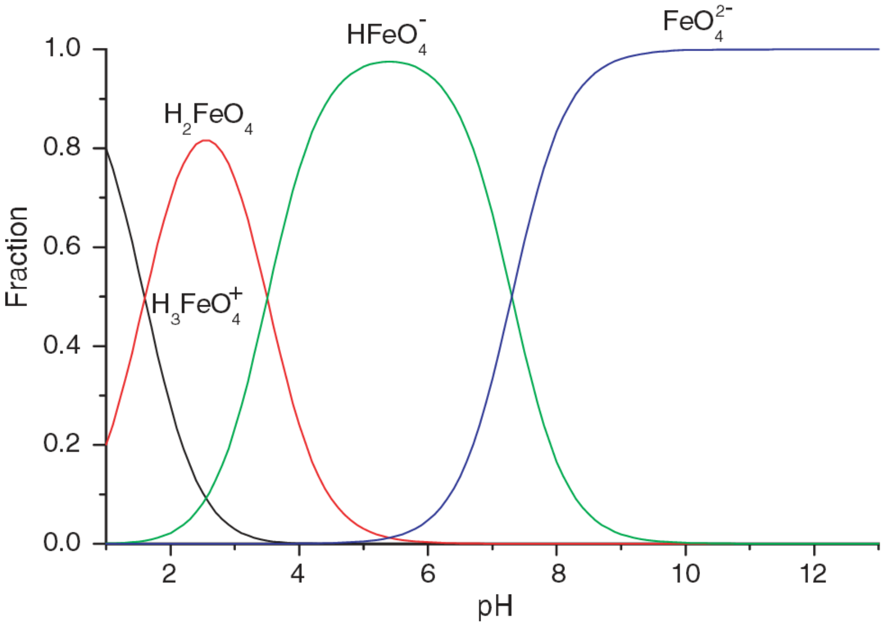

Figure 2: Fe(VI) species under various pH conditions[41,42,31,43]

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).

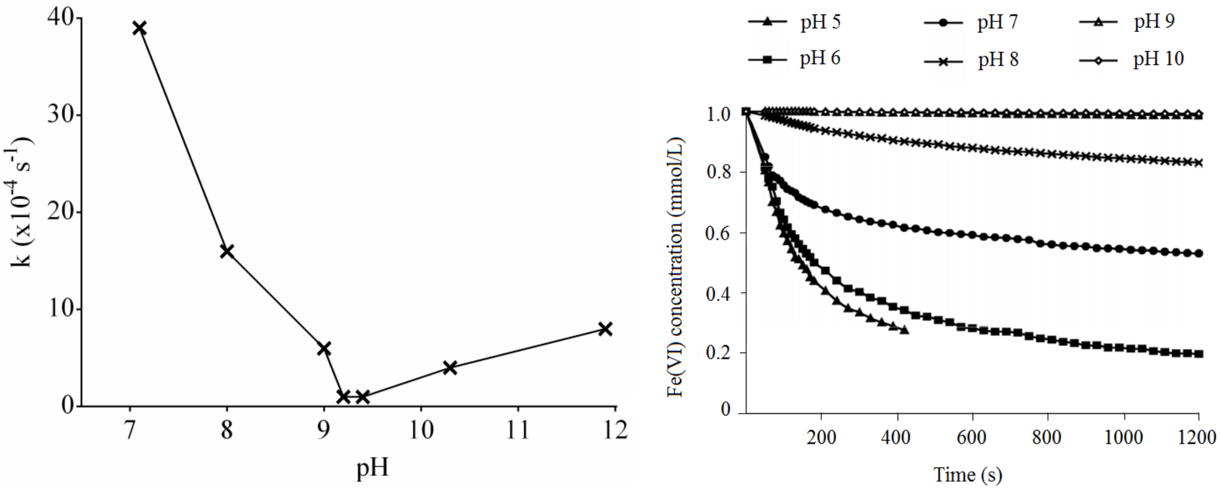

Figure 3: Fe(VI) decomposition rate under different pH conditions (left)[43] *and the spontaneous decomposition of Fe(VI) under different pH conditions (right)*[30]

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].

3.1.2 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.

3.1.3 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 3.1.2).

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, $[\mathrm{EDCs}]_0 = 0.15$ 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.

3.2 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 REACTIVITY OF FERRATES WITH POPs

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].

For our study, representatives of POPs were selected 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, penta- and hexachlorobenzene (PeCB, HCB) and PCB.

The results of the reactivity of ferrates with HCH, PCP and PCDD/F were published in impact journals. The abstracts and conclusions of these papers are listed below. One full article is presented as an example at the end.

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 can conclude that ferrates are not applicable for their removal.

4.1 Degradability of hexachlorocyclohexanes in water using ferrate (VI)

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, 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 K2O 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)

4.2 Degradability of pentachlorophenol using ferrate(VI) in contaminated groundwater

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)

4.3 Chemical degradation of PCDD/F in contaminated sediment

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)

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

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 $4948\ M^{-1}s^{-1}$ 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.

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.

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

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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

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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.

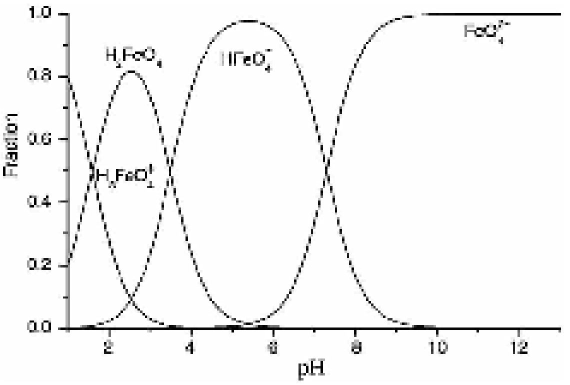

Figure 1 | Relative amounts of Fe(VI) species under various pH conditions (Carr *et al.* 1985; Rush *et al.* 1996; Sharma 2002; Li *et al.* 2005).

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 (±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 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$^{\cdot+}$ 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$^{\cdot+}$ of 34,000 M^{-1}·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}·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 ≥ 6) it can be assumed that PCP was present in the fully dissociated form (pKa ~ 4.7).

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

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):

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

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:

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

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

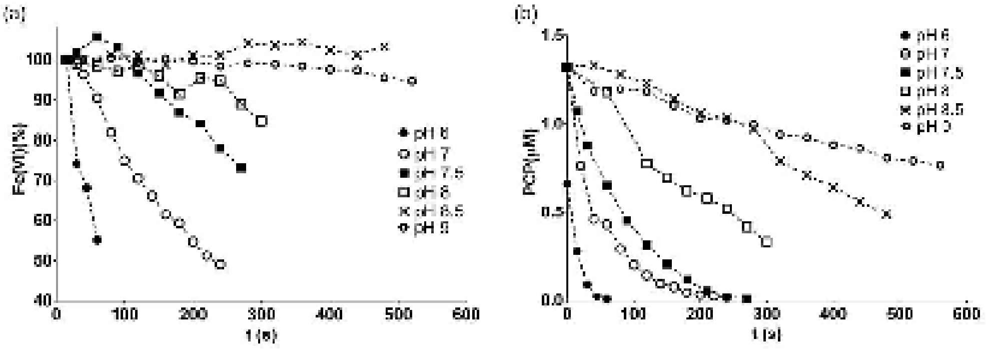

Figure 2 | Time profile of Fe(VI) (a) and PCP (b) concentrations under different pH conditions.

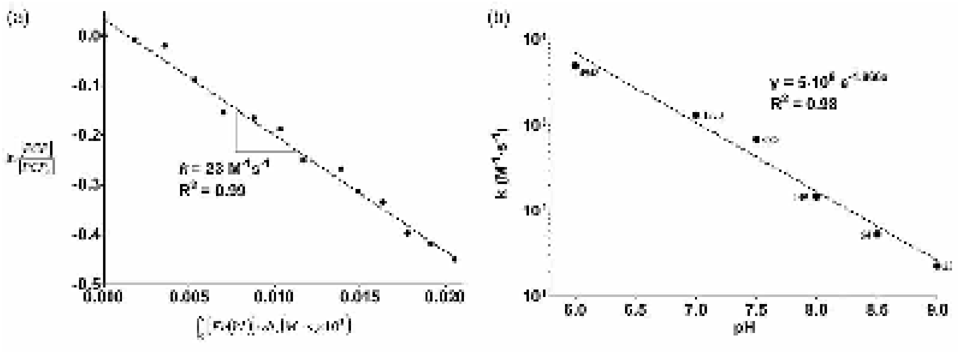

Figure 3 | (a) An example of a graphical expression of Equation (2) for pH 9; (b) the dependency of rate constant *k* on pH.

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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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 expecred 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. Details about PCP degradation are presented in this thesis presentation.

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

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