

Degradability of chlorophenols using ferrate(VI) in contaminated groundwater

M. Homolková¹ · P. Hrabák¹ · M. Kolář² · M. Černík¹

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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.

Keywords Degradability · Ferrate · Fe(VI) · Pentachlorophenol · Chlorophenols · Complex contaminated water

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✉ M. Homolková
martina.homolkova@tul.cz

¹ Faculty of Mechatronics, Informatics and Interdisciplinary Studies & Institute for Nanomaterials, Advanced Technologies and Innovations, Technical University of Liberec, Studentská 1402/2, Liberec 461 17, Czech Republic

² Regional Centre of Advanced Technologies and Materials, Palacký University in Olomouc, Šlechtitelů 11, 783 71 Olomouc, Czech Republic

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 As their utilization has been replaced by more effective chemicals, less chlorinated CPs are of a limited use today (Exon 1984).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 Igbinsosa 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/>).

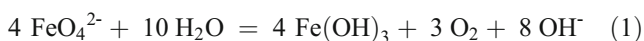
When advanced analytical techniques were developed, the widespread distribution of CPs was revealed in the environment (soil, water and air samples, food products, human and animal tissues and body fluids), even in remote areas (e.g. PCP was detected in the tissues of polar bears and ringed seals), originating 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 Igbinsosa 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.atsdr.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 Igbinsosa 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 Igbinsosa 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 FeO₄²⁻ is significantly slower and can be described by the Eq. (1) (Jiang and Lloyd 2002; Sharma 2002).



Ferrate(VI) ion, FeO₄²⁻, 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 FeO₄²⁻ 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 % K₂FeO₄) 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 ⁵⁷Fe 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 FeO₄²⁻ 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 $^{\circ}\text{C}$.

Pentachlorophenol $^{13}\text{C}_6$ (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 $\mu\text{g/l}$ sum of DDD (dichlorodiphenyldichloroethane), DDE (dichlorodiphenyldichloroethylene) and DDT (dichlorodiphenyltrichloroethane), 30 mg/l sum of chlorobenzenes, 750 $\mu\text{g/l}$ BTEX (benzene, toluene, ethylbenzene and xylenes), 20 $\mu\text{g/l}$ sum of chloroethylenes and 107 $\mu\text{g/l}$ 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 $\text{ANC}_{4.5}$ and $\text{BNC}_{8.3}$ 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 $\text{H}_3\text{BO}_3/\text{NaOH}$ 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 $\mu\text{g/l}$). 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 $\text{H}_3\text{BO}_3/\text{NaOH}$, 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

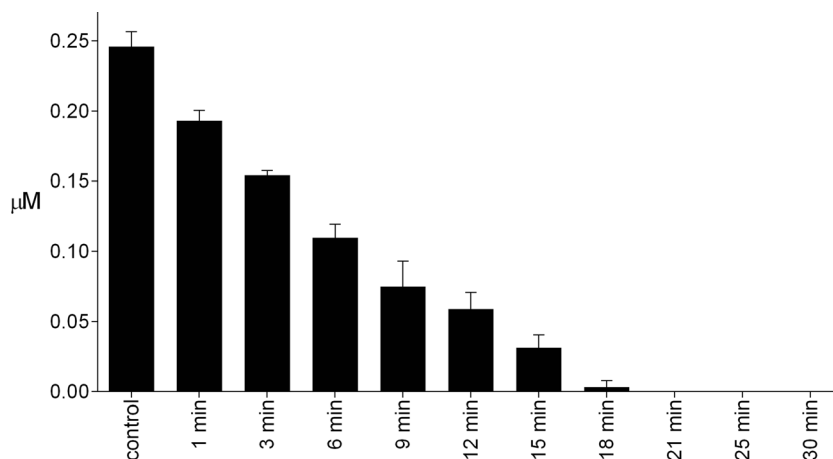
CPs (acetylated derivatives) were determined in hexane extracts using a Trace 1310 gas chromatograph fitted with a triple quadrupole tandem TSQ 8000 mass spectrometry detector (Thermo ScientificTM). Fe(VI) concentrations were determined using a Lambda 35 UV/VIS absorption spectrometer (PerkinElmer Instruments) with molar absorptivity of $1150 \text{ M}^{-1} \text{ cm}^{-1}$ 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 FeO₄²⁻ 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 FeO₄²⁻ 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 FeO₄²⁻. The results obtained by the treatment of less pure ferrate, LAC A, were in a good agreement with an already described trend (Olaniran and Igbinsosa 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 FeO₄²⁻ 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 FeO₄²⁻ 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 FeO₄²⁻ (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

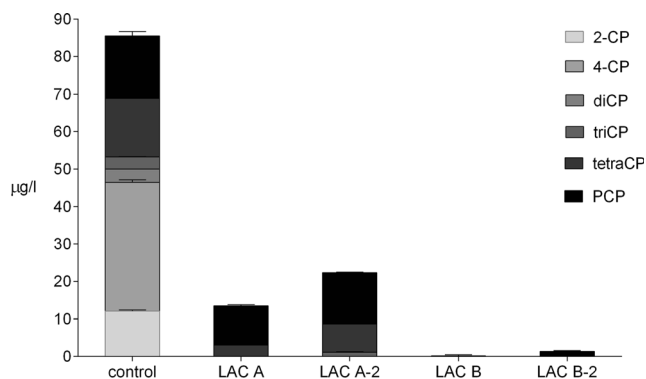


Fig. 2 Concentration of CPs in real groundwater after 24 h in the presence of approximately 290 μM LAC A or LAC B ferrates; LAC A-2 and LAC B-2 are half ferrate concentrations (mean+standard deviation; $\mu\text{g/l}$)

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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