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

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: H₃FeO₄⁺, H₂FeO₄⁻, HFeO₄⁻ and FeO₄²⁻ 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% K₂FeO₄) 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 K₂FeO₄ 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 FeO₄²⁻ for the kinetic experiments and 500 μM FeO₄²⁻ 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 0.45μm membrane, after vigorous stirring and ultrasound treatment, resulting in a concentration of 15 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 NH₄HCO₃ (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 NH₃. 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](https://iwaponline.com/wst/article-pdf/75/1/189/456727/wst075010189.pdf)
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) \( (k = 1.2 \times 10^6 \text{M}^{-1} \text{s}^{-1} \text{at pH 7}) \) and formed a green coloured radical ABTS\(^{3+} \) 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 \( \mu \)m 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 \( \mu \)M and 250 \( \mu \)M of PCP and Fe(VI), respectively. Each sample was prepared in quadruplicate.

<table>
<thead>
<tr>
<th></th>
<th>Demineralized water</th>
<th>PCP stock solution (54 ( \mu )M)</th>
<th>Fe(VI) stock solution (500 ( \mu )M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank water</td>
<td>40 mL</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Blank ferrate</td>
<td>20 mL</td>
<td>–</td>
<td>20 mL</td>
</tr>
<tr>
<td>Base PCP</td>
<td>20 mL</td>
<td>20 mL</td>
<td>–</td>
</tr>
<tr>
<td>Reaction</td>
<td>–</td>
<td>20 mL</td>
<td>20 mL</td>
</tr>
</tbody>
</table>

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 \( \mu \)m 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\(^{3+} \) of 34,000 \( \text{M}^{-1} \cdot \text{cm}^{-1} \) 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 \( \text{M}^{-1} \cdot \text{cm}^{-1} \) 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 \( \text{pH} < 2.5 \) 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 \( \mu \)m, 2.1 \( \times \)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 a 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).

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

(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):

\[
\ln \left( \frac{[PCP]}{[PCP_0]} \right) = -k[Fe(VI)]t
\]

(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:

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

(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
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)

<table>
<thead>
<tr>
<th></th>
<th>PCP (μM)</th>
<th>Cl$^-$ (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank water</td>
<td>$&lt;10^{-5}$</td>
<td>5.6</td>
</tr>
<tr>
<td>Blank ferrate</td>
<td>$&lt;10^{-5}$</td>
<td>5.6</td>
</tr>
<tr>
<td>Base PCP</td>
<td>26.54 ± 3.12</td>
<td>12.42 ± 1.13</td>
</tr>
<tr>
<td>Reaction samples</td>
<td>(26.7 ± 14.6)×10$^{-4}$</td>
<td>143.02 ± 3.39</td>
</tr>
</tbody>
</table>
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 concluded 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: $k (\text{M}^{-1} \text{s}^{-1}) = 5 \times 10^8 \exp(-1.866 \text{pH})$. 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 ($k > 10^3 \text{M}^{-1} \text{s}^{-1}$), 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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