Degradability of hexachlorocyclohexanes in water using ferrate (VI)
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ABSTRACT

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

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

INTRODUCTION

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

HCH exists in nine stereoisomeric forms, the most common being α-HCH, β-HCH, γ-HCH and δ-HCH. γ-HCH, also known as lindane, has been used as both an agricultural insecticide and a pharmaceutical and veterinary treatment for lice and scabies (Abhilash & Singh 2013). It is estimated that around 600,000 tonnes of lindane were produced globally over the last century, the vast majority being used in agriculture (Mrema et al. 2013). The World Health Organisation classifies lindane as being ‘moderately hazardous’ and the use of technical HCH was banned between the 1970s and 1980s. HCH was further listed under the Stockholm Convention in 2009. Although the use of lindane as a pesticide was prohibited over 30 years ago, background concentrations can still be found in water and soil (Ren et al. 2006).

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

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Pesticides are traditionally removed from contaminated ground/wastewater by coagulation, flocculation, membrane separation or adsorption on activated carbon (Nitoi et al. 2013). In fact, these technologies do not degrade the contaminants themselves but transfer them onto other matrices, which must then be further treated themselves. One example of a common degradation procedure is that of catalytic reductive dechlorination, which yields benzene (C₆H₆) as the major final product. While there are many publications on reductive transformation and degradation of HCHs (e.g. Wang et al. 2009; Singh et al. 2012), there are relatively few concerning oxidation methods (Cao et al. 2013). Potassium ferrate (K₂FeO₄) is a strong oxidant, disinfectant and coagulant that has a stronger oxidation potential under moderately acidic pH conditions than any other chemical commonly used for wastewater treatment (chlorine, hypochlorite, chlorine dioxide, ozone, hydrogen peroxide, dissolved oxygen or permanganate). Furthermore, there are no known side-effects and no potentially hazardous pollutants.

Ferrates, the higher oxidation states of iron Fe(IV, V and VI) have attracted much interest in recent years due to their involvement in the treatment of a diverse range of common environmental pollutants (Sharma et al. 2008b; Al-Abduly & Sharma 2014). Potassium ferrate (K₂FeO₄) is a strong oxidant, disinfectant and coagulant (Filip et al. 2011; Prucek et al. 2013). Other by-products of chlorination and their health effects have been further summarised by Skaggs et al. (2008). In comparison, the by-product of ferrate oxidation is the ferric ion Fe(III), which is environmentally benign and a micronutrient for plant life:

$$2 \text{FeO}_2^{2-} + 5 \text{H}_2\text{O} = 2 \text{Fe}^{3+} + 3/2 \text{O}_2 + 10 \text{OH}^- \quad (1)$$

Conversely, ferrates are the most expensive oxidant and require very special handling. Despite this, ferrates are presently considered a highly promising ‘green’ water treatment oxidant, disinfectant and coagulant (Filip et al. 2011; Prucek et al. 2013).

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

This study represents part of a wider feasibility study for the remediation of complex contamination of water from former pesticide production areas. As stated above, the number of previous studies examining degradability of POPs using ferrates is limited, despite ferrates being considered by many authors to be an ideal wastewater treatment reagent and POPs being priority pollutants. The present study examines the applicability of Fe(VI) for HCH degradation/removal and especially the role of pH. Furthermore, for comparison, zero-valent iron nanoparticles (nZVI) were used to assess the effect of a similar amount of Fe at opposite extremes of valence (Fe⁰). HCH degradation was expected in nZVI systems in accordance with a previous study (Wang et al. 2009).

**MATERIALS AND METHODS**

**Chemicals**

The potassium ferrate (produced as part of our research project) used in our study had a composition (as determined through a combination of $^{57}$Fe Mössbauer spectroscopy and atomic absorption spectroscopy) of 83.6 wt% K₂FeO₄, 6.5 wt% Fe₂O₃ and 9.9 wt% potassium oxides with traces of silicon, aluminium and zirconium. Stock solutions (0.5–2 mM) of Fe(VI) were prepared by dissolving the solid sample in cooled demineralised water (obtained using a PURELAB flex system (ELGA LabWater, Prague, Czech Republic)). Owing to the inhomogeneity of the ferrate material, it was not possible to calculate precise ratios in advance; hence, final concentrations of the Fe(VI) stock solutions were calculated retrospectively after photometric measurement. For this reason, the ratios in repeat experiments varied slightly. All of the Fe(VI) stock solutions were used within 15 min of preparation.

A saturated stock solution of HCH was prepared by dissolving standard HCH (isomer mixture $\alpha:\beta:\gamma:S = 1:1:1:1$; purity >99.3%; Fluka, Sigma–Aldrich Co., Prague, Czech Republic) in demineralised water. This was filtered through a 0.45 µm filter after vigorous stirring for 3 days. The stock solution was then stored in a refrigerator at 5°C.
Standard NANOFER 25P nZVI (NANO IRON, s.r.o., Olomouc, Czech Republic) was used in the form of a dry powder preserved in an inert nitrogen atmosphere. The particles were without surface modification and had an average size of 50 nm, average surface area of 20–25 m²/g and a narrow size distribution of 20–100 nm. The content of iron was high, ranging between 80 and 90 wt%. An aqueous suspension of Fe(0) was prepared from the powder at a ratio of 1.4 nZVI:water, which yielded a suspension with an nZVI content of 0.2 g Fe(0)/1 ml.

Methods

Each experiment was performed in a 100 ml reaction flask. The specified amount of demineralised water or H₂BO₃/ NaOH buffer (depending on the experiment) was placed into the flask, spiked with 10 ml of HCH stock solution and the required amount of ferrate stock solution was added. The total reaction volume was always 50 ml. Unless stated otherwise, the solutions were extracted (shaking for 30 min at 150 rpm) with 10 ml of hexane the following day. Each set of samples included control and base samples. The controls were treated in the same way as the samples (same composition and simultaneous extraction) but without addition of the ferrate in order to distinguish the influence of pH or time from the influence of the ferrate. The base samples comprised demineralised water spiked with HCH and were extracted straight after preparation to determine the initial concentration of HCH without pH or time influence. All of the experiments were undertaken in triplicate and at ambient temperature.

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

Analytical methods

HCH and higher chlorinated ChB (tri-, tetra-, penta- and hexachlorobenzene) were determined in hexane extracts using a Trace 1310 gas chromatograph fitted with a triple quadrupole tandem TSQ 8000 mass spectrometry detector (Thermo Scientific TM, Pragolab, Prague, Czech Republic). Unknown peaks of the mass spectra were compared with the National Institute of Standards and Technology library. In some cases, peaks were identified as potential reaction by-products. Less than tri-chlorinated benzenes (dichlorobenzenes, chlorobenzene and benzene) were quantified by the static head-space method using a CP-3800 gas chromatograph with a Saturn 2200 ion trap mass spectrometry detector (Varian, Amedis, Prague, Czech Republic). Fe(VI) concentrations were determined using a Lambda 35 UV/VIS absorption spectrometer (PerkinElmer Instruments, PE Systems, Prague, Czech Republic) with molar absorptivity of 1,150 M⁻¹cm⁻¹ at 505 nm (Licht et al. 2007). Measurements of pH were carried out using a pH50 pH meter (Giorgio Bormac, Chromservis, Prague, Czech Republic), which was calibrated using standard pH 4.01, 7.00 and 10.01 buffers.

RESULTS AND DISCUSSION

HCH reactivity with ferrate

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

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

Because the unbuffered, aqueous ferrate solution tends to increase its pH value (Equation (1)), a further step was taken to distinguish the role of ferrate and the particular influence of increased pH. A second experiment was conducted wherein three sets of reactors were prepared containing water buffered to pH 9, 10 or 11 with no ferrate...
added. Concentrations of HCH and ChB were measured after 0, 5, 24, 48 and 72 h (Figure 2). In the pH 10 and pH 11 reactors the concentration of HCH decreased significantly over time, accompanied by an increase in TCBs (1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene; data not shown), the trend being most obvious at pH 11. A decrease in the concentration of HCH was not confirmed at pH 9 (Figure 2). These results led to the assumption that the HCH transformation/degradation shown in Figure 1 may have been a consequence of increased pH in the reaction system only.

As there was no significant transformation of HCH at pH 9 (Figure 2) this pH appeared suitable for other experiments with ferrate as any transformation/degradation observed would have been caused by the ferrate itself. The comparison of the control with the test solution with a molar ratio of ferrate to HCH of 17:1, both buffered to pH 9, indicated no decrease in HCH (Figure 3, left). This suggested that pH, and not ferrate, may be the main driver in the HCH degradation observed in Figure 1.

As the ferrate reactivity is known to be higher at lower pH levels (Lee et al. 2004), it was anticipated that HCH degradation would increase under more acidic conditions. To confirm this, the previous experiment was repeated under neutral (pH 7) and slightly acidic (pH 5) conditions. The ferrate to HCH molar ratio remained the same, i.e., 17:1. Each reactor (containing buffered water and HCH) was stirred vigorously because the ferrate reacts instantly...
in this pH range. For the same reason the ferrate stock solution was added gradually (one-tenth of the volume added at a time). The results (Figure 3, right) indicated no degradation of HCH and no formation of TCBs or other ChBs.

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

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

**HCH reactivity with nZVI**

Unlike in the ferrate system, only a minor pH shift was observed during the reaction of the HCH with nZVI. This suggested that the HCH should not have been influenced by pH in the same manner as in the case of the ferrates. The results of the nZVI experiments indicated a degradation of HCH (Figure 4). Benzene and chlorobenzene were found in this system as products of reductive dechlorination.

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

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

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