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Application of chemical oxidation to remediate HCH–contaminated soil under batch and flow through conditions

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Abstract

This is the first study describing the chemical oxidation of hexachlorocyclohexanes (HCHs) in contaminated soil under water-saturated and unsaturated flow through conditions. Soil contaminated with β–HCH (45 mg. kg^{-1}) and γ–HCH (lindane, 25 mg. kg^{-1}) was sampled from former lindane waste storage site. Efficiency of following treatments was tested at circumneutral pH: H_2O_2 alone, H_2O_2/Fe^{II}, $Na_2S_2O_8$ alone, $Na_2S_2O_8/Fe^{II}$, and $KMnO_4$. Experimental conditions (oxidant dose, liquid/solid ratio and soil granulometry) were first optimized in batch experiments. Obtained results revealed that increasing dose of H_2O_2 improved the oxidation efficiency while in $Na_2S_2O_8$ system, maximum HCHs were removed at 300 mM. However, oxidation efficiency was slightly improved by Fe^{II}–activation. Increasing the solid/liquid ratio decreased HCH removal in soil samples crushed to 500 µm while an opposite trend was observed for 2 mm samples. Dynamic column experiments showed that oxidation efficiency followed the order $KMnO_4$ > $Na_2S_2O_8/Fe^{II}$ > $Na_2S_2O_8$ whatever the flow condition, whereas the removal extent declined at higher flow rate (e.g. ~50% by $KMnO_4$ at 0.5 mL/min as compared to ~30% at 2 mL/min). Both HCH removal and oxidant decomposition extents were found higher in saturated columns than the unsaturated ones. While no significant change in relative abundance of soil mineral constituents was observed before and after chemical oxidation, more than 60% of extractable organic matter was lost after chemical oxidation, thereby underscoring the non–selective behavior of chemical oxidation in soil. Due to the complexity of soil system, chemical oxidation has rarely been reported under flow through conditions, and therefore our findings will have promising implications in developing remediation techniques under dynamic conditions closer to field applications.

Keywords: HCHs; Lindane; Soil remediation; chemical oxidation; column; saturated and unsaturated conditions.

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1. Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs), an international environmental treaty, recently (in 2009) classified three hexachlorocyclohexanes (HCHs) namely α–HCH, β–HCH, and γ–HCH (lindane) as POPs (Vijgen et al. 2011). Due to their global usage, strong toxicity, environmental persistence and bio-accumulative nature, HCHs appear as ubiquitous pollutants in the environment (Li et al. 2011, Vijgen et al. 2011). Among HCHs, lindane is one of the widely investigated organochlorine pesticide in the last few decades. It has been estimated that the global usage of lindane was 600,000 tons as broad-spectrum pesticide in the second half of the 20th century (Vijgen et al. 2011, Voldner & Li 1995, Willett et al. 1998). Moreover, production of one ton of lindane generates approximately 6–10 tons of waste containing other HCH isomers. According to a recent estimation, 4.8 million tons of lindane manufacturing waste may still be present in the environment (Manonmani 2011). Disposal of such huge waste has led to the creation of many dumpsites, which ultimately become the source of HCH contamination. Present study also concerns HCH contaminated soil (located in Northeastern France) that was encapsulated at a former lindane waste storage site. Due to the spread of contamination from this storage site, traces of lindane were detected in ground water and the surrounding soil.

Due to the associated environmental concerns, there is growing interest in the development of new and effective technologies to remove HCHs. In recent years, advanced oxidation processes (AOPs) are showing promising potential to remove POPs from contaminated matrices (Cheng et al. 2016, Usman et al. 2016a). Various AOPs have been investigated to remove HCHs including persulfate oxidation (Cao et al. 2008), ozonation (Begum & Gautam 2012), H_2O_2 assisted UV photo-degradation (Nienow et al. 2008, Nitoi et al. 2013), persulfate activated by electrochemical processes (Wacławek et al. 2015), cobalt-activated peroxymonosulfate system (Wacławek et al. 2016) and Fe^{II}/UV/peroxymonosulfate system

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(Khan et al. 2016a, b). However, all these studies were performed in aqueous solutions. Our recent batch (no flow) study was the first work to report chemical oxidations of HCHs in contaminated soils (Usman et al. 2014). We reported an efficient degradation of α, γ, β and δ–HCH in spiked sand as well as real contaminated soil by chemical oxidation (hydrogen peroxide, persulfate and permanganate) (Usman et al. 2014). Recently, Peng and co-workers (2015) investigated the use of persulfate activated by various methods including heat at 40 °C, high pH and Fe^{III}–EDTA reagent to remove lindane in spiked soil (not real contaminated soil).

In addition to the scarcity of the data in contaminated soils, to the best of our knowledge, chemical oxidation has never been applied to remove HCHs in soil columns neither under water saturated nor under unsaturated conditions. Therefore, present study was aimed to investigate the chemical oxidation of HCH contaminated soil under flow through conditions. Indeed, column experiments with suitable soil/water ratio can provide operational parameters that are closer to *in–situ* or field applications. It should be noted that chemical oxidation has rarely been studied under unsaturated conditions (vadose zone) even for other organic pollutants (Laurent et al. 2012, Palmroth et al. 2006). As a matter of fact, chemical oxidation-based remediation has been almost exclusively used for treating contaminated groundwater or aquifer.

For this purpose, various chemical oxidants (hydrogen peroxide, persulfate and permanganate) were applied to degrade HCHs in tested soil. Prior to column tests, experimental conditions (oxidant dose, liquid/solid ratio and granulometry) were optimized in no-flow system. Then, we performed dynamic column experiments under saturated and unsaturated conditions. The influence of experimental conditions (type and dose of oxidant, flow rate or residence time, granulometry and iron activation) on oxidation efficiency was

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also investigated under flow-through conditions. HCHs in organic extracts were quantified by using Gas Chromatography–Mass spectrometry (GC–MS).

2. Experimental section

2.1. Soil samples and chemical reagents

All reagents used in present study were of analytical grade and are detailed in Supplementary material. Contaminated soil used in the present study was sampled from a former gravel pit that was backfilled with waste of lindane and is located in Sierentz-Alsace (SA) in Northeast of France. Thousands of tons of lindane-contaminated waste were disposed in that pit by French lindane-manufacturing industry (PCUK) from 1965–1970. This industry ceased functioning in 1974 and the pit was later confined by using waterproof capsule to avoid further spread of contamination. Total weight of the encapsulated HCH contaminated soil and waste was estimated to be 112 000 tons (Dubearnes 2006). French environmental agency (ADEME) is responsible for monitoring of tested site where traces of lindane were detected in 2003 at the base of capsule and in groundwater despite its encapsulation. Sampled soil contains relatively fine-grained fractions (19.2% of clay and 13.8% of fine silt) with organic matter (7%), total organic carbon (4.5%), and C/N ratio of 13.6. The pH of soil is relatively higher (~8.05) which might be linked to its high $CaCO_3$ contents (19.5%). A detailed description about properties of the tested soil is presented elsewhere (Usman et al. 2014).

2.2. Investigation of oxidation reaction under batch conditions

In first step, batch (no-flow) experiments were used to optimize experimental conditions for H_2O_2 and persulfate to degrade HCHs in contaminated soil. All oxidation tests are summarized in Table 1 and general procedure is explained in Supplementary material. First experiment evaluated the degradation efficiency at various oxidant doses including (i) H_2O_2

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alone (900 mM) without iron activation (H_2O_2) and Fenton oxidation (H_2O_2/Fe^{II}) by using (ii) 200 mM H_2O_2 + 20 mM soluble Fe^{II} (dose A), (iii) 900 mM H_2O_2 + 90 mM soluble Fe^{II} (dose C), (iv) sodium persulfate alone (600 mM) without iron activation ($Na_2S_2O_8$), and activated persulfate ($Na_2S_2O_8/Fe^{II}$) by using (v) 100 mM $Na_2S_2O_8$ + 50 mM soluble Fe^{II} (dose A) (vi) 600 mM $Na_2S_2O_8$ + 300 mM soluble Fe^{II} (dose C). For comparison, results corresponding to 600 mM H_2O_2 + 60 mM soluble Fe^{II} (dose B), 300 mM sodium persulfate + 150 mM soluble Fe^{II} (dose B) were borrowed from Usman et al. (Usman et al. 2014). Blank experiments were also performed in water under the same conditions but without any oxidant, to study possible degradation of the HCHs. An oxidant:Fe molar ratio equal to 10:1 (H_2O_2) and 2:1 (persulfate) was chosen in soil slurry according to the previous findings (Usman et al. 2014).

Effect of solid/liquid was evaluated by comparing chemical oxidation at different sample loadings i.e. 5 g, 10 g and 20 g of SA soil (Table 1). For each set of experiment, granulometry was also changed by sieving the soil samples through different mesh sizes (500 µm, 2 mm and 5 mm) to demonstrate the impact of particle size. Soil samples having particle size of 500 µm were obtained by sieving soil samples through 2 mm mesh size followed by grinding.

2.3. Chemical oxidation under flow through conditions

Column experiments were conducted by using a glass chromatographic column of 120 mm length and 25 mm internal diameter. The main characteristics of the columns are presented in Table 2. Chemical oxidation was performed under saturated and unsaturated conditions (see Table 1 for conditions). In general procedure, contaminated soil samples corresponding to a dry mass of 20 g were packed in columns. After packing, the column was cautiously wetted upward with the Milli–Q water (Millipore) to obtain saturated conditions. Once the column was saturated, the column was fed upwards at the same constant flow rate with soluble Fe^{II} solution followed by the oxidant solution (open system). Firstly, experiments were conducted

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by using soil samples having particle size of 500 µm, but columns were clogged up after some time probably due to small particle size. But, column experiments conducted with soil samples sieved at 2 mm did not show any clogging issues. Therefore, further column experiments were performed by using soil samples sieved at 2 mm. Five oxidation treatments including H_2O_2, H_2O_2/Fe^{II}, $Na_2S_2O_8$ and $Na_2S_2O_8/Fe^{II}$ (detailed in Table 1) were firstly tested using the same oxidant doses as in no-flow and by keeping a liquid/solid ratio constant (i.e. 5 g : 20 ml in batch, and 20g : 80 ml in column). Additionally, permanganate ($KMnO_4$) alone (90 mM) was tested under flow through conditions based on the results of previous no-flow study (Usman et al. 2014). Blank experiments (prepared in similar way) were conducted by injecting water in soil packed column in a continuous mode at the same constant flow rate. Experiments were conducted under two different flow rates (0.5 and 2 mL/min) in order to investigate the influence of oxidant residence time on the HCH degradation in column. The flow rate was checked several times and was found constant. Once whole solution was injected, the solid samples were freeze-dried to remove water and then analyzed as explained below.

Experiments were then conducted to evaluate the impact of oxidant dose onto oxidative degradation of β–HCH under flow through conditions (Table 1). For this purpose, experiments were performed under two conditions (i) with iron activation and (iii) without iron activation by using three different oxidant doses including 100 mM, 300 mM and 600 mM of $Na_2S_2O_8$, and 200 mM, 600 mM and 900 mM of H_2O_2. When activated, one porous volume of a solution containing soluble Fe^{II} (60 mM) was dosed in columns before injecting oxidant solution at the same flow rate (i.e. 0.5 ml/min, Table 1). Experiments were also conducted by using 30 mM and 90 mM of $KMnO_4$ alone.

Experiments were also performed under unsaturated soil conditions (Table 1). Soil columns, with a length of 120 mm and diameter of 25 mm, identical to those employed in saturated

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conditions were packed with 20 g of contaminated soil. Column conditions are detailed in Table 2. Then, these columns were fed by sprinkling of oxidant solutions with a constant flow rate of 0.5 mL/min: i) $KMnO_4$ (30 mM), ii) $Na_2S_2O_8$ (100 mM), iii) H_2O_2 alone (600 mM) and iv) H_2O_2 activated by iron (600 mM H_2O_2 + 60 mM soluble Fe^{II}). The column was continuously weighed using a balance located underneath the column, to ensure a constant porosity and to avoid a significant change in water content along the experiment. Three replicates were analyzed from each column. All results were expressed as a mean value of the three values and standard deviation of the three replicates was less than 5%. All experiments were performed at room temperature (20–22 °C). The column test was stopped and the packed soil was analyzed, once all injected volume was exhausted. It should be noted that HCH concentration was monitored in solid phase through extraction/analysis procedures (as explained in the following section), and therefore no classical breakthrough curve (C/C_0 as a function of PV, porous volume) can be plotted in this study. Analysis of the column effluent (after liquid–liquid extraction with chloroform) revealed that outflow concentration of HCHs was almost zero, thereby underscoring the absence of HCH mobilization from the column. Concentration of remaining H_2O_2 and $Na_2S_2O_8$ oxidant were determined by iodometric titration, and $KMnO_4$ concentrations by colorimetric titration (Barnes et al. 2005, Brumblay 1971).

2.4. Extraction and analysis

The freeze-dried samples were extracted in chloroform and were analyzed by GC–MS as detailed in supplementary material.

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3. Results and discussion

3.1. Optimization of HCH degradation under no-flow conditions

Sampled soil (SA), crushed to 500 µm, was analyzed to determine the HCH content and results obtained by GC–MS revealed the presence of γ–HCH (lindane, 25 mg. kg^{-1}) and β–HCH (45 mg. kg^{-1}). These soil samples were subjected to chemical oxidation at various oxidant doses (Table 1) under no-flow conditions without pH adjustment. Degradation of both isomers was calculated per their initial contents and concerned data after 24 h of reaction is represented in Figure 1. For comparison purposes, values corresponding to dose B of H_2O_2/Fe^{II} and $Na_2S_2O_8/Fe^{II}$ were borrowed from a previous study (Usman et al. 2014). Almost no HCH degradation was observed in blank experiments. In H_2O_2/Fe^{II} treatments, dose C exhibited stronger removal of both β–HCH (~70%) and γ–HCH (~90%) (Fig. 1). Use of $Na_2S_2O_8/Fe^{II}$ (dose B and C) also removed up to ~40% of β–HCH and ~90% of γ–HCH. Increasing oxidant dose exhibited positive influence on oxidation efficiency in H_2O_2/Fe^{II} treatments while no pronounced effect was observed beyond dose B of $Na_2S_2O_8/Fe^{II}$ in persulfate oxidation. Similarly, no significant improvement in degradation efficiency was reported beyond an optimum oxidant dose during radical based oxidation of polycyclic aromatic hydrocarbons in contaminated soils that was correlated to the radical scavenging (Lemaire et al. 2013). It is worthy to note that both oxidants when applied without iron activation also effectively degrade both β–HCH (37% and 30% by H_2O_2 and $Na_2S_2O_8$ respectively) and lindane (75% and 89% by H_2O_2 and $Na_2S_2O_8$ respectively). This strong degradation without Fe^{II} activation could be linked to the presence of native iron minerals (2.47 wt% of Fe_2O_3) or transition metals (Table S1 in Supplementary material) present in the tested soil that might catalyze the chemical oxidants (Ahmad et al. 2010, Anipsitakis & Dionysiou 2004, Usman et al. 2014). Moreover, oxidants can also contribute by directly

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oxidizing the pollutants *via* non-radical pathways or direct electron transfer process as explained previously (Usman et al. 2014). These results also reveal that Fe^{II} activation did not result in pronounced increase in oxidation efficiency that might be caused by its precipitation at relatively high pH of tested soil (Matta et al. 2008, Tamura et al. 1980). A very slight decrease in pH (from 8.05 to 7.90) was observed after introduction of reactants that stayed almost constant during the whole course of reaction probably due to the soil's high carbonate content (~20%) or buffering capacity. It should be noted that an acidic pH is required to keep Fe^{II} in soluble form for optimum efficiency of traditional Fenton oxidation (Safarzadeh-Amiri et al. 1996, Usman et al. 2016a). In previous reports, the soluble Fe^{II} was neither able to catalyze Fenton oxidation (Usman et al. 2012a) nor persulfate oxidation (Usman et al. 2012b) at circumneutral pH to treat PAHs in former coking plant soils. Therefore, it was suggested that iron minerals or chelating agents could be used instead of soluble Fe^{II} to catalyze chemical oxidation at circumneutral pH (Usman et al. 2012a, b). This initial acidification in traditional Fenton oxidation could be costly, impractical in soils due to their high buffering capacity and could negatively affect the soil quality and successive vegetation (Laurent et al. 2012, Sirguey et al. 2008). Therefore, present study was performed without pH adjustment to avoid initial acidification and/or injection of multiple reagents (chelating agents or iron minerals). Furthermore, acidification of large volume in soils would be impractical for column experiments or *in-situ* high scale applications.

Obtained GC–MS chromatograms were almost identical before or after oxidation, suggesting that no new reaction products can be detected under our analytical conditions. This may be partially due to the very fast reaction kinetics of sulfate and hydroxyl radicals with possible by-products (if formed), and/or lower concentration (below the detection limit) of these unknown compounds. In aqueous solution, Nitoi and co-workers (2013) revealed the formation of chlorinated by-products such as hexachlorobenzene and trichlorobenzene during

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the photo-Fenton oxidation of lindane, which disappeared completely after 4 h of reaction. Complete degradation was also achieved during oxidation of lindane by Fe^{II}-activated persulfate (2,3,4–trichlorophenol was formed as a primary by-product but was subsequently degraded over time) (Cao et al. 2008) or oxidation of γ–HCH by thermally-activated persulfate (Peng et al. 2015).

It should be noted that non-selective behavior of chemical oxidation could also degrade the non-target organic compounds. Therefore, a significant loss of extractable organic matter (60–80%) was observed after chemical oxidation in the investigated soil. However, contents of metal oxides like Al_2O_3, TiO_2, CaO and P_2O_5 remained almost similar (Table S1 in Supplementary material) whatever the used oxidant. In experiments using Fe^{II} as catalyst, higher iron content was observed in the treated soil (Table S1).

Our results also indicate that β–HCH was more recalcitrant than lindane as previously observed (Usman et al. 2014). This recalcitrant behavior of β–HCH could be explained by its higher chemical and metabolic stability due to the absence of axial–orientated chlorines and lowest Henry's law constant (Beurskens et al. 1991, Johri et al. 1998). Due to its higher recalcitrance and greater concentration in the tested soil, rest of the experiments focused only on the degradation of β–HCH.

Experiments were also conducted with different solid loading (solid/liquid ratio) and particle sizes, in order to optimize the experimental conditions for column studies. For this purpose, chemical oxidation treatments (Table 1) were applied at various soil loadings (5 g, 10 g and 20 g) and particle sizes (500 µm, 2 mm and 5 mm) (Fig. S1 in Supplementary material). Obtained results for the soil sample having 500 µm (Fig. S1a) indicated that degradation of β–HCH decreased with an increase in solid loading. This was expected because HCH content and oxidant demand (radical scavenging) increased with an increase in sample size (from 5 to

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20 g) that would decrease oxidation efficiency. On the other hand, an opposite trend was observed for samples with 2 mm particle size where degradation efficiency increased with an increase in solid loading (Fig. S1b). Quantification of initial β–HCH content revealed a difference of 30 ppm between soil samples having particle size of 500 µm (43 ppm) and 2 mm (73 ppm) which suggests that 40% of β–HCH was lost when 2 mm samples were grinded to obtain 500 µm. Soil samples sieved at 2 mm contain a higher initial pollutant content with higher availability that ultimately could enhance the degradation. Availability of the pollutant was found as the main limiting factor controlling the efficiency of subsequent chemical oxidation (Jonsson et al. 2007, Usman et al. 2012a, 2016b). Thus, increasing the sample size (from 5 g to 20 g) for 2 mm samples increases such free fraction of β–HCH that is more easily degradable. On the other hand, no general degradation trend was observed during oxidation of different solid loading at 5 mm (Fig. S1c), probably due to the higher heterogeneity of the tested samples (with larger particle size, 5 mm).

3.2. Investigation of HCH degradation under flow through conditions

Firstly, column experiments (Table 1: column experiments *I*) were performed by using soil samples having 500 µm but severe clogging-up was observed due to lower particle size and poor hydraulic conductivity or permeability in column. Clogging problem persisted even when the tested soil was mixed with sand (30% w/w) to improve its porosity. Therefore, further column experiments were conducted by using soil samples having 2 mm particle size where no such problems were observed. Efficiency of chemical oxidation was tested under saturated flow through conditions by injecting oxidant solution at two different flow rates (0.5 mL/min and 2 mL/min) and the obtained results are presented in Figure 2. The permanganate was tested under flow through conditions based on the results of a previous no-flow study (Usman et al. 2014). The decomposition extents of oxidants were determined for *Column experiment I* (Table 1) at 0.5 ml/min by measuring the final concentration in column effluents

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at the end of reaction. However, no breakthrough curve (i.e. oxidant concentration versus porous volume number or time) could be determined. The decomposition extent of oxidant lies at 100% for H_2O_2 or H_2O_2/Fe^{II}, 32 % and 56% for $Na_2S_2O_8$ and $Na_2S_2O_8/Fe^{II}$, respectively, and only 30 % for $KMnO_4$.

Almost no degradation was observed in blank experiments where no oxidant was used. No traces of β–HCH in outflow solution (i.e. column effluent) were observed stating the absence of its mobilization from column. Obtained results (Fig. 2) indicated that oxidation efficiency followed this order $KMnO_4$ > $Na_2S_2O_8/Fe^{II}$ > H_2O_2/Fe^{II} > $Na_2S_2O_8$ > H_2O_2 at 0.5 mL/min (Fig. 2). A similar trend was observed ($KMnO_4$ > $Na_2S_2O_8/Fe^{II}$ > $Na_2S_2O_8$) but with lower degradation efficiency when flow rate increased to 2 mL/min. Lower degradation at high flow rate could be attributed to lower residence time of oxidants in columns. But injection of hydrogen peroxide (H_2O_2/Fe^{II} or H_2O_2 alone) at higher flow rate did not yield any results due to the significant release of heat and creation of strong pressure in column ultimately leading to its blockage. Despite the same solid/liquid ratio and oxidant dose used in batch as well as in dynamic column experiments, a higher degradation extent was observed in column experiments. The greater efficiency in column could be correlated to the difference in experimental conditions between no-flow and flow regimes. Indeed, oxidant injected at a constant flow rate reaches progressively the column bed, in contrast to the single addition in batch. This could avoid parasite reactions (e.g. self-decomposition of H_2O_2, scavenging effects, etc.), which generally occur when a high amount of oxidant (with or without catalyst) comes into contact spontaneously with soil. Similar observations were reported in the batch system when sequential addition of oxidant was found more efficient than single addition (Kong et al. 1998, Tseng et al. 2012). Analyses of tested soil after chemical oxidation revealed that metal oxides (Table S1) represented similar trend as in batch conditions (relative abundance of Al_2O_3, Fe_2O_3, TiO_2 and P_2O_5 did not significantly change and almost similar

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increase in Na_2O when $Na_2S_2O_8$ was used). However contrary to batches, soil iron content did not increase when soluble Fe^{II} was used, probably because it flushed out in column effluents. It is worthy to note that entire system (water + solid) in batches is subjected to freeze-drying prior to extraction/analysis, and thus dissolved components are also retained in the post-treated soil.

Although $KMnO_4$ has been shown to be the least reactive oxidant to degrade HCHs under no-flow conditions as demonstrated in our previous study (Usman et al. 2014), it becomes the most active one under flow through conditions. This discrepancy in efficiency of $KMnO_4$ under batch and column conditions could not come from the stabilization of HCH isomers in MnO_2 generated from the decomposition of $KMnO_4$ (Kao et al. 2008, Yan & Schwartz 1999), since the latter is supposed to occur in both batch and column systems. It may be, however, possible that formed MnO_2 interferes with $KMnO_4$ and thus influences the oxidation efficiency, and this "*side reaction*" must be different in batch *vs* column flow systems. Indeed, contact between parent compound (e.g. oxidant) and oxidation byproducts may be likely reduced under flow-through conditions, since byproducts could be flushed out from the column. Although this hypothesis is the most plausible one, this issue needs further investigations. It should be noted that preliminary extraction tests and GC–MS analyses (data not shown) showed no impact of addition of synthetic MnO_2 on the recovery of HCHs during extraction.

Obtained results indicated that oxidation efficiency was decreased with an increase in flow rate or with a decrease in residence time (Fig. 2), suggesting that kinetic limitations may occur at a high flow rate (2 mL/min). In the absence of physical diffusion, preferential pathways or stagnant zones, the extent of reaction that occurs in column is controlled by chemical oxidation kinetic and residence time. The higher the flow rate the lesser the contact time between oxidant and target contaminant, and therefore the lesser the oxidation reaction

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efficiency. To test the impact of kinetic limitation in column, Damköhler number (Da) that represents the ratio of hydrodynamic residence time to characteristic time for chemical reaction in the column is generally used (Hanna et al. 2012, Rusch et al. 2010). Unfortunately, the lack of kinetic data of HCH in soil (oxidation was determined only at 24 h) and mass transfer rate in column does not allow the estimation of Da number. Nevertheless, the present findings showed clearly that a lower flow rate (0.5 mL/min) could ensure a sufficient residence time to reach greater oxidation extent (e.g. ~ 50 % using $KMnO_4$).

Further experiments were conducted by using various oxidant doses (detailed in Table 1: column experiments *II*) injected at a flow rate of 0.5 mL/min. Obtained results (Fig. 3) indicate that application of 600 mM of H_2O_2 resulted in higher oxidation of β–HCH (17–29%) as compared to the 200 mM (16–17%) or 900 mM (8%) of oxidant. Relatively poor degradation of β–HCH at elevated oxidant dose of 900 mM could be linked to the scavenging of $OH^{\bullet}$ radicals by H_2O_2 that becomes of great importance at much higher concentration (Wang et al. 2000). Degradation efficiency was almost similar (16–17%) if H_2O_2 (200 mM) was applied with or without iron activation. But, Fe^{II} activation of 600 mM H_2O_2 resulted in higher degradation (29%) than without iron addition (17 %). On the other hand, Fe^{II} activation has a negative impact on oxidation efficiency of $Na_2S_2O_8$ at various oxidant doses except for 600 mM. This could be attributed to the rapid decomposition of persulfate due to Fe^{II} activation, and scavenging effect of sulfate radicals by Fe^{II} before it has an opportunity to react with the target contaminants (Romero et al. 2010, Zhao et al. 2013). Scavenging of sulfate radicals by Fe^{II} especially at higher concentration can be detrimental for oxidation efficiency (Romero et al. 2010). In case of $Na_2S_2O_8$, the most effective dose seems to be the 600 mM with 50% of β–HCH degradation. However, a degradation extent of 34% was obtained with lower dose of 100 mM (6x less than 600 mM) without iron activation that seems as more economical dose if degradation efficiency/oxidant dose is considered. The

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$KMnO_4$ showed strong efficiency to degrade β–HCH with similar oxidation efficiency at both doses (48% and 49% of degradation with 30 mM and 90 mM respectively) and thus rendering 30 mM more economical. To the best of our knowledge, no data about HCH oxidation in column is available in the literature and therefore it is difficult to make a fair comparison of our findings with the literature.

Experiments were then conducted under unsaturated conditions by using the most efficient systems obtained in saturated systems, i.e. $KMnO_4$ (30 mM), $Na_2S_2O_8$ (100 mM), iii) H_2O_2 alone (600 mM) and iv) H_2O_2/Fe^{II} (600 mM H_2O_2 + 60 mM soluble Fe^{II}) (Fig. 4). However, columns designated to H_2O_2 application (with or without catalyst) were not analyzed due to the very strong reaction leading to column plugging and ultimately the overflow from the column. Indeed, the sprinkled H_2O_2 immediately decomposes at the top of soil, which creates a kind of foam preventing circulation of the sprinkler solution.

Obtained results (Fig. 4) indicated that $KMnO_4$ resulted in 24% of β–HCH degradation as compared to the 18% by $Na_2S_2O_8$ (Fig. 4a). It should be noted that single reagents ($Na_2S_2O_8$ or $KMnO_4$) caused such degradation and that could be advantageous in soils where injection of multiple reactants could be difficult. It was also observed that regardless of the oxidant, degradation of β–HCH is more important for saturated conditions than unsaturated conditions. This could be explained by the presence of gas phase and/or preferential pathways through soil column under unsaturated conditions (*e.g.* porosity is lower in unsaturated columns, table 2). These conditions could decrease soil/oxidant contact because of the less proportion of the soil available for oxidation reaction and it will ultimately lead to lower pollutant degradation. This behavior was further confirmed by measuring the oxidant consumption in columns at the end of reaction. As shown in Figure 4b, lower decomposition extents of oxidant were noted for unsaturated columns as compared to saturated conditions. As mentioned above, the available literature severely lacks deep investigations on the chemical oxidation under

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saturated *vs* unsaturated conditions, to be compared with our present findings. Nevertheless, other reports on the distribution of heavy metals (Plassard et al. 2000) and leaching of herbicides (Weber & David 1982) showed that the extent of reaction (Lewis & Sjöstrom 2010) was more important under saturated-flow conditions than that under unsaturated-flow conditions.

4. Conclusion

Tested soil was sampled from former HCH waste storage facility and was found contaminated with β–HCH and lindane (γ–HCH). It was subjected to chemical oxidation by using hydrogen peroxide and sodium persulfate, both with and/or without soluble Fe^{II}, and permanganate. Experimental conditions were first optimized under no-flow conditions for successive chemical oxidation under flow through conditions. This study represents the following important points:

i– *No-flow experiments:* Chemical oxidation resulted in significant degradation of HCHs in contaminated soils without any identified by-products under our analytical settings. As expected, soluble Fe^{II} was unable to significantly activate H_2O_2 and $Na_2S_2O_8$ at circumneutral pH in soil. Increasing oxidant dose improved oxidation efficiency till an optimum amount. The β–HCH showed higher recalcitrance than lindane. Degradation of β–HCH was decreased with an increase in solid loading for soil samples crushed to 500 µm, while an opposite trend was observed for soil samples sieved through 2 mm. No general trend was, however, observed for soil samples at 5 mm.

ii– Saturated column experiments: Experiments were conducted under saturated flow through conditions at two different flow rates (0.5 and 2 ml/min) and at different oxidant doses. Higher β–HCH degradation was observed at 0.5 mL/min due to higher residence time of oxidants in column. Moreover, saturated columns also resulted in higher HCH degradation

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than no-flow conditions especially for permanganate that was the most effective oxidant under flow through conditions.

iii– *Unsaturated column experiments:* Significant degradation of β–HCH was observed under unsaturated conditions by using permanganate and persulfate. Lower HCH removal as well as oxidant decomposition extents were observed in unsaturated columns as compared to saturated conditions. Obtained results indicated that such degradation was achieved by using single reagents (sodium persulfate or permanganate alone) which could be advantageous in soils where injection of multiple reagents could be problematic. As a matter of fact, the use of chemical oxidation has been rarely reported under flow through conditions to remediate contaminated soils due to the complexity of system. Although a small difference in degradation performance was observed in saturated-flow *vs.* unsaturated-flow conditions, our findings showed that chemical oxidation is effective to degrade HCHs in both investigated systems. Therefore, these results are very promising to develop strategies to remediate subsurface soils (i.e. unsaturated conditions) as well as contaminated aquifer (i.e. saturated conditions).

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Table 1: Details of chemical oxidation treatments employed in no-flow and column studies.

Batch experiment I: Effect of oxidant dose			
Oxidant	**Test**	**Oxidant dose**	**Catalyst dose (Fe^{II})**
Hydrogen peroxide (H_2O_2)	-	900 mM	0 mM
Fenton (H_2O_2/Fe^{II})	A	200 mM	20 mM
	B	600 mM	60 mM
	C	900 mM	90 mM
Sodium persulfate ($Na_2S_2O_8$)	-	600 mM	0 mM
Activated Persulfate ($Na_2S_2O_8/Fe^{II}$)	A	100 mM	50 mM
	B	300 mM	150 mM
	C	600 mM	300 mM
Reference (Blank)	Blank	No oxidant	0 mM

Batch experiment II: Effect of solid loading/particle size				
Solid loading	**Particle size**	**Oxidant**	**Oxidant dose**	**Catalyst dose (Fe^{II})**
5 g **or** 10 g **or** 20 g	500 µm **or** 2 mm **or** 5 mm	H_2O_2	600 mM	0 mM
		H_2O_2/Fe^{II}	600 mM	60 mM
		$Na_2S_2O_8$	300 mM	0 mM
		$Na_2S_2O_8/Fe^{II}$	300 mM	150 mM
		Blank	No oxidant	0 mM

Column experiment I: Effect of flow rate (saturated conditions)					
Solid loading	**Flow rate**	**Particle size**	**Oxidant**	**Oxidant dose**	**Catalyst dose (Fe^{II})**
20 g	0.5 mL/min **or** 2 mL/min	500 µm **or** 2 mm **or** 500 µm samples mixed with sand (30% w/w)	H_2O_2	600 mM	0 mM
			H_2O_2/Fe^{II}	600 mM	60 mM
			$Na_2S_2O_8$	300 mM	0 mM
			$Na_2S_2O_8/Fe^{II}$	300 mM	60 mM
			$KMnO_4$	90 mM	0 mM
			Blank	No oxidant	0 mM

Column experiment II: Effect of oxidant dose (saturated columns)					
Solid loading	**Flow rate**	**Particle size**	**Oxidant**	**Oxidant dose**	**Catalyst dose (Fe^{II})**
20 g	0.5 mL/min	2 mm	H_2O_2	200 mM	0 mM **or** 60 mM
				600 mM	0 mM **or** 60 mM
				900 mM	0 mM **or** 60 mM
			$Na_2S_2O_8$	100 mM	0 mM **or** 60 mM
				300 mM	0 mM **or** 60 mM
				600 mM	0 mM **or** 60 mM
			$KMnO_4$	30 mM	0 mM
				90 mM	0 mM
			Blank	No oxidant	0 mM

Column experiment III: Chemical oxidation under unsaturated columns					
Solid loading	**Flow rate**	**Particle size**	**Test**	**Oxidant dose**	**Catalyst dose (Fe^{II})**
20 g	0.5 mL/min	2 mm	H_2O_2	600 mM	0 mM **or** 60 mM
			$Na_2S_2O_8$	100 mM	0 mM
			$KMnO_4$	30 mM	0 mM
			Blank	No oxidant	0 mM

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Table 2: Summary of the column characteristics.

	Experimental I and II (saturated columns)	**Experimental III (unsaturated columns)**
Soil weight, g	20	20
Column section, cm^2	4.9	4.9
Height of bed, cm	3.5	3.5
Bed density ρ,g cm^3	1.16	1.16
Pore volume Vp, mL	7.8	5.9
Flow rate, ml min^{-1}	0.5; 2	0.5
Porosity, θ	0.45	0.34
Q, cm min^{-1}	0.1; 0.4	0.1
Velocity, cm min^{-1}	0.22; 0.88	0.29

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Figure captions:

Figure 1: Degradation of β–HCH and lindane after chemical oxidation by: H_2O_2 alone (900 mM) without iron activation and Fenton oxidation (H_2O_2/Fe^{II}) by using 200 mM H_2O_2 + 20 mM soluble Fe^{II} (dose A), 600 mM H_2O_2 + 60 mM soluble Fe^{II} (dose B), 900 mM H_2O_2 + 90 mM soluble Fe^{II} (dose C), sodium persulfate alone (600 mM) without iron activation ($Na_2S_2O_8$), and activated persulfate ($Na_2S_2O_8/Fe^{II}$) by using 100 mM $Na_2S_2O_8$ + 50 mM soluble Fe^{II} (dose A), 300 mM $Na_2S_2O_8$ + 150 mM soluble Fe^{II} (dose B) and 600 mM sodium persulfate + 300 mM soluble Fe^{II} (dose C). Quantification of HCH isomer was performed by GC–MS. Values corresponding to the dose B of H_2O_2/Fe^{II} and that of $Na_2S_2O_8/Fe^{II}$ were borrowed from previous study (Usman et al. 2014).

Figure 2: Degradation of β–HCH in contaminated soil (sieved through 2 mm mesh size) under saturated column conditions at two different flow rates (0.5 mL/min and 2 mL/min) after chemical oxidation by: 600 mM H_2O_2, Fenton oxidation by using 600 mM H_2O_2 + 60 mM soluble Fe^{II} (H_2O_2/Fe^{II}), 300 mM sodium persulfate alone ($Na_2S_2O_8$), activated persulfate by using 300 mM sodium persulfate + 60 mM soluble Fe^{II} ($Na_2S_2O_8/Fe^{II}$) and 90 mM of $KMnO_4$. Quantification of HCH isomer was performed by GC–MS.

Figure 3: Effect of oxidant dose on the degradation of β–HCH in contaminated soil (sieved through 2 mm mesh size) under saturated column conditions (flow rate of 0.5 mL/min) as evaluated with following chemical oxidant doses: 200 mM H_2O_2 (dose A), 600 mM H_2O_2 (dose B), 900 mM H_2O_2 (dose C), 100 mM $Na_2S_2O_8$ (dose A), 300 mM $Na_2S_2O_8$ (dose B), 600 mM $Na_2S_2O_8$ (dose C), 30 mM $KMnO_4$ (dose A) and 90 mM $KMnO_4$ (dose B). For comparison, soluble Fe^{II} (60 mM) was also used as a catalyst with all tested quantities of H_2O_2 and $Na_2S_2O_8$. Quantification of HCH isomer was performed by GC–MS.

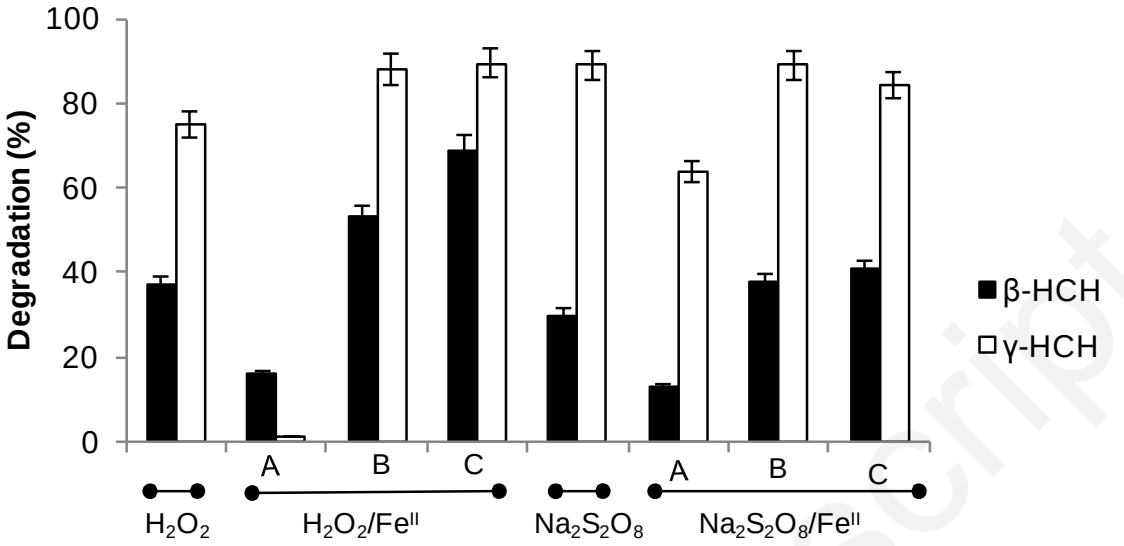
Figure 4: Comparison of (a) degradation of β–HCH in contaminated soil (sieved through 2 mm mesh size) and (b) decomposition extent of oxidant as a function of column under

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saturated vs. unsaturated conditions tested with following two oxidants: 100 mM sodium persulfate ($Na_2S_2O_8$) and 30 mM potassium permanganate ($KMnO_4$). Unsaturated conditions were maintained by sprinkling oxidant solutions on contaminated soils with a constant flow rate of 0.5 mL/min.

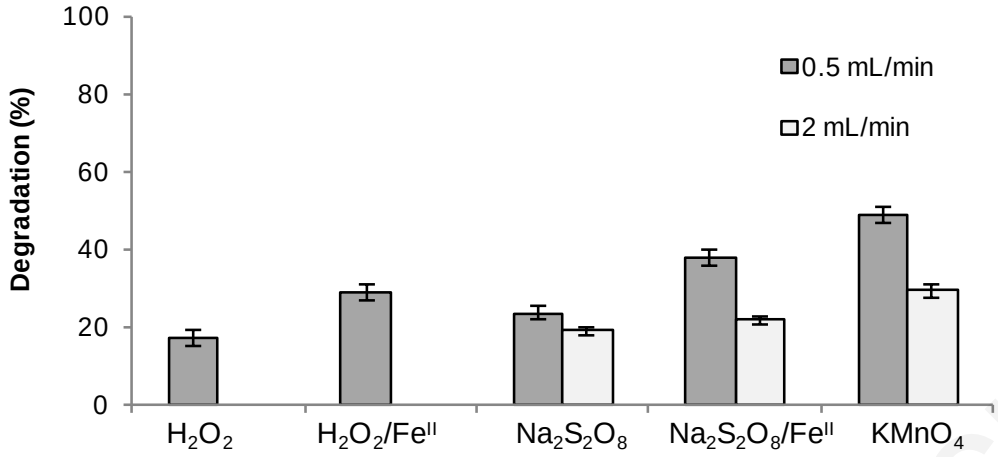
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Figure 1:



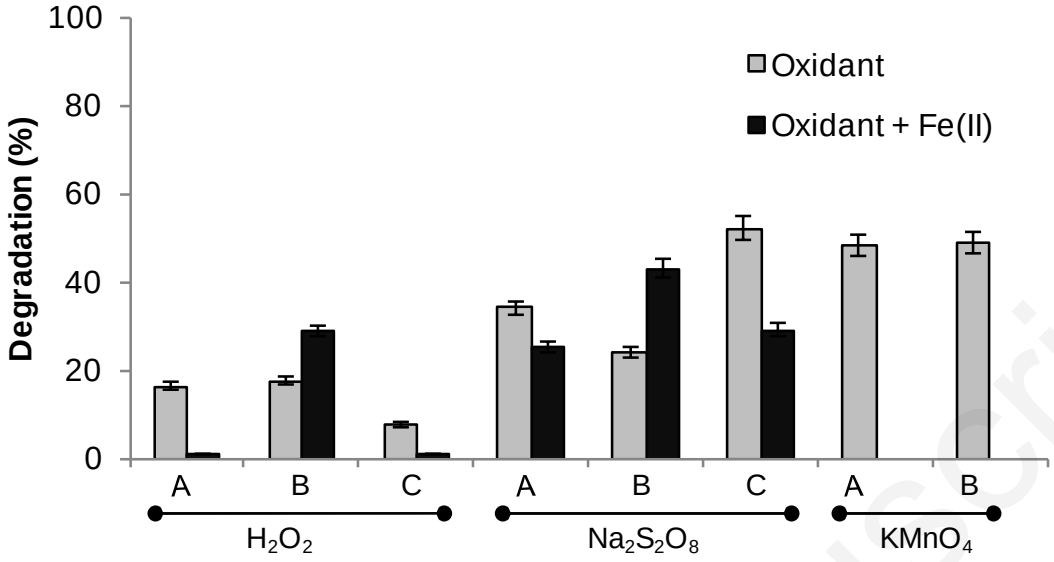
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Figure 2:



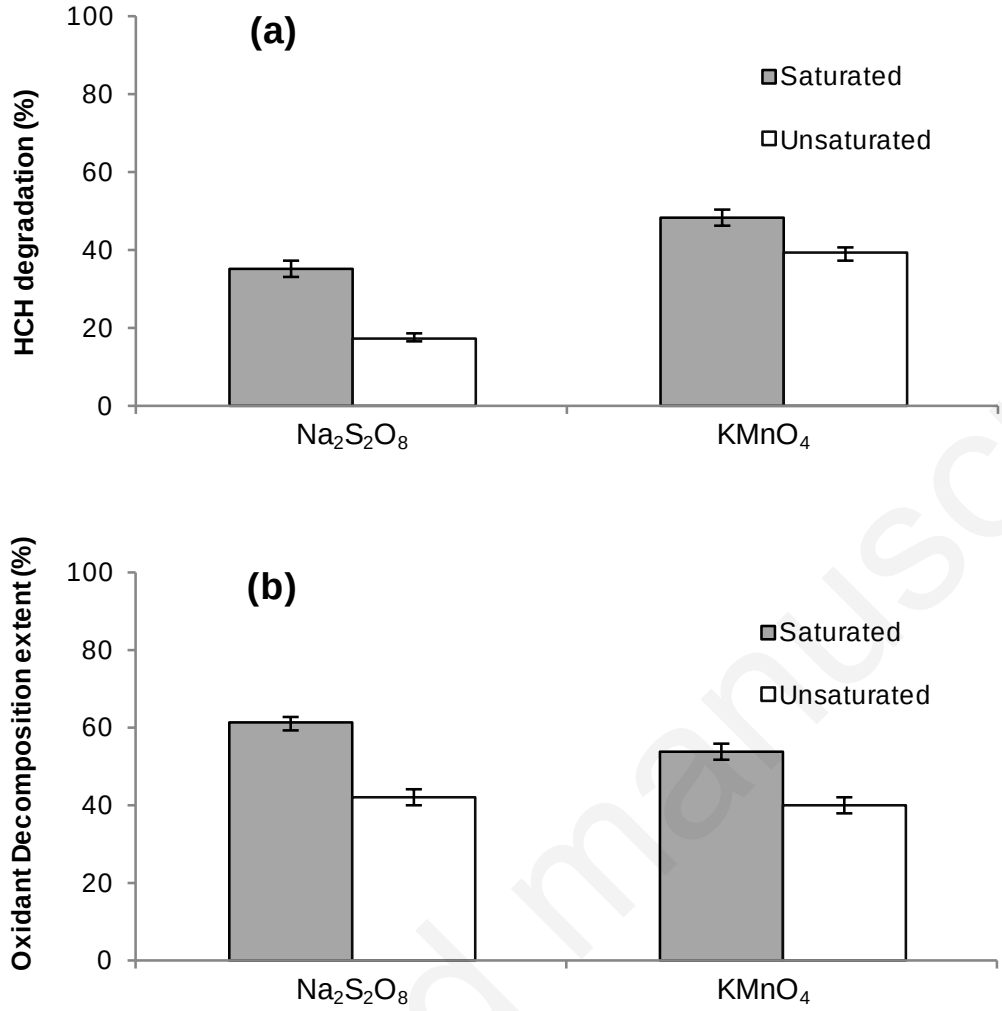
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Figure 3:



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Figure 4:



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