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Remediation of an aged PCP-contaminated soil by chemical oxidation  
under flow-through conditions

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## Abstract

In this study the oxidation of pentachlorophenol (PCP) in an aged contaminated soil was performed under both water-unsaturated and water-saturated conditions using potassium permanganate (PM), potassium persulfate (PS) and hydrogen peroxide (HP). Overall, the results of PCP removal extent and oxidant decomposition indicated that the water content in column has no significant impact on the oxidation performance. The increase in flow rate from 0.025 to 2.5 mL min<sup>-1</sup> decreased the oxidant decomposition as well as the PCP degradation extent, except for HP that is highly reactive. Kinetic limitations in column may explain the effect of residence time of oxidant on the degradation performance. Consistently, re-circulation of oxidant solutions in a closed loop system improved the oxidation efficiency and oxidant decomposition extents in case of PS and PM, but not for HP. Surprisingly, attempts to enhance the PCP availability in soil by using solubility agents or by heating did not improve the degradation efficiency in soil. The presence of methyl- $\beta$ - cyclodextrin (M- $\beta$ -CD) affects only the decomposition rate of HP, which is positively correlated with M- $\beta$ -CD concentration. High persistence of HP could be advantageous where delivery of oxidants to zone-source of contamination can be limited by their high reactivity. Collectively, these results may have strong implications for the application of chemical oxidation under field conditions, particularly where oxidant injection mode in saturated or unsaturated zones is crucial in determining the remediation performance.

**Key words:** pentachlorophenol; contaminated soil; oxidation; column; mobilization.

## 1. Introduction

Pentachlorophenol (PCP) is a synthetic organic compound firstly produced in 1930 in the United States [1]. It has been used worldwide as a wood preservative and biocide till the end of 20<sup>th</sup> century. Accidental spillage and improper disposal of PCP containing solutions has resulted in soil and water contamination [2]. PCP is listed as priority pollutant by USEPA [3] and it is extremely toxic to humans and many living organisms. PCP mainly affects liver, thyroid, immune system, reproductive system, and the developing organisms. The EPA and IARC classify pentachlorophenol as probable human carcinogen [4]. PCP is soluble in water and usually found in surface and ground water. Physical and chemical properties of the compound suggest that it is hardly evaporated into the atmosphere and tends to adsorb on soil particles [5].

There are several technologies developed for remediation of PCP-contaminated soils, including biological, chemical and thermal treatment (incineration). Biological treatment is an environmentally-friendly technology. However, PCP is persistent to microbial degradation due to its highly chlorinated organic nature and biodegradation rates are reported to be slow and incomplete at high concentrations [6]. Slow or absent biodegradation are usually explained by the presence of soil organic matter, clay minerals and moisture, as well as by insufficient number and poor survival of PCP degraders [7,8]. The incineration is an energy consuming technology, accompanied by the emission of hazardous compounds [9].

*In situ* chemical oxidation (ISCO) of PCP can be relatively rapid, easy in application and economical remediation technology. ISCO involves the introduction of chemical oxidants directly into the contaminated source. The most common oxidants are hydrogen peroxide, persulfate and permanganate. Hydrogen peroxide (HP) ( $E^0 = 1.8 \text{ V}$ ) is generally activated by ferrous ion ( $\text{Fe}^{2+}$ ) (Fenton's reagent) generating more strong oxidants - hydroxyl radicals ( $\text{OH}^\bullet$ ) with redox potential of 2.8 V [10]. However, acid conditions are needed ( $\text{pH} < 3$ ) to avoid the precipitation of  $\text{Fe}^{2+}$  and maintain the generation of  $\text{OH}^\bullet$  radicals [11,12]. Since the initial adjustment of pH could be costly

and impractical on large scale due to buffering capacity of soils, the use of iron oxides instead of soluble  $\text{Fe}^{2+}$  present clear advantages for *in situ* soil remediation [13]. In addition, soil acidification can certainly enhance negative impacts of chemical oxidation on soil quality [14]. Persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) (PS) itself is a strong oxidant and can be activated chemically or thermally to form the sulfate radical  $\text{SO}_4^{\cdot-}$ , stronger oxidant with redox potential of 2.6 V [15]. Permanganate (PM) is efficient oxidant in a wide range of pH with redox potential of 1.68 V, which degrades organic pollutants through non-radical mechanism and, therefore, can be employed without activation [16].

Although chemical oxidation of PCP has been previously studied [9,11,17-19], remediation of PCP-contaminated soil by chemical oxidation under flow-through conditions has been scarcely investigated, and particularly for PS and PM systems. Indeed, column tests with suitable soil/water ratio can provide more accurate operational parameters for field applications. In addition, column experiments allow evaluating the effect of non-equilibrium and hydrodynamic parameters on the oxidation performance in continuous flow-through conditions. Therefore, this study aims to evaluate the efficiency of chemical oxidation in PCP-contaminated soil under dynamic flow-through conditions, using three different oxidation systems (PM, PS and HP). The investigated PCP-contaminated soil was sampled from a timber mill in Waipa district of Waikato Region, New Zealand and then characterized. Preliminary tests were conducted in batch conditions in order to evaluate PCP oxidation by different doses of oxidants in absence and presence of activators at near neutral pH, e.g. Fe-based nanoparticles ( $\text{Fe}^0$  or magnetite). Two approaches including water-saturated conditions and water-unsaturated conditions were performed in column dynamic experiments. Because non-reacted oxidant can be flushed out of system in continuous flow-through conditions and then ultimately affects the oxidant extent, recirculation of injected solution (in closed loop) was also carried out in water-saturated column tests. The PCP concentrations were measured in both column effluent and soil bed, whereas the breakthrough curves of oxidant were determined as a function of time or porous volume.

## Materials and methods

### 2.1. Materials

Iron sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 99.5%), sodium borohydride ( $\text{NaBH}_4$ , 98%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 50%), sodium hydroxide ( $\text{NaOH}$ , *extra pure*) and 1,10 phenantroline monohydrochloride ( $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{HCl} \cdot \text{H}_2\text{O}$ , 97%) were purchased from *Acros Organics Chemicals*, UK. Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ,  $\geq 99.0\%$ ) were purchased from *Sigma Aldrich*, USA. Potassium hydroxide ( $\text{KOH}$ , 85%) and potassium nitrate ( $\text{KNO}_3$ , 99%) were purchased from *Merck KgaA*, Germany. Potassium permanganate ( $\text{KMnO}_4$ , 99%) was provided by *Prolabo*, France. Pentachlorophenol (97%) and phenol ( $\leq 99\%$ ) were analytical grade and purchased from *Supelco* (*Sigma-Aldrich Corporation*). Organic acids (oxalic, 99.99%; glyoxalic, 50 wt % in  $\text{H}_2\text{O}$ ; acetic, 99.99%; maleic  $\geq 99\%$ , formic, 98%), hydroxylamine chlorhydrate ( $\text{H}_3\text{NO} \cdot \text{HCl}$ , 99%) and methyl- $\beta$ -cyclodextrin (M- $\beta$ -CD) were provided by *Sigma-Aldrich*. Methanol (99.9%) were purchased from *Biosolve*, France and used as received. Absolute ethanol was purchased from *VWR Chemicals*. Deionized water was produced by *Milli-Q system* from *Millipore*.

$\text{Fe}^0$  and magnetite nanoparticles used in this study were synthesized according to the methods described elsewhere in Rybnikova et al. [20] and Schwertmann and Cornell [21], respectively.

### 2.2. Soil preparation and characterization

Contaminated soil used in this study was obtained from a timber mill in Waipa district of Waikato Region, New Zealand. Prior to experiments, soil was dried, ground and passed through 1 mm (18 mesh) sieve. Obtained fraction was characterized by the *Institute en Santé Agro Environnement* (ISAE), Combourg, France. Soil characteristics are presented in Table 1. According to particle size distribution, the soil is classified as loamy sand. The soil is slightly carbonated and has a pH of 7.2. It contains 1.5% of organic matter and high concentrations of iron ( $9.8 \text{ g kg}^{-1}$ ) and exchangeable cations ( $1.5 \text{ g kg}^{-1}$ ). The total PCP concentration in soil is  $6 \text{ mg kg}^{-1}$ , which is above the quality

criteria of soil for agricultural use in New Zealand and considered as a soil with serious risk in New Zealand as well as in Europe [22].

**Iron speciation in soil.** Iron speciation was performed using methods described by Van Bodegom et al. [23]. Total Fe content was determined by the extraction of 2 g of soil with 10 N HCl. Amorphous iron was extracted with oxalate solution (0.113 M sodium oxalate/0.086M oxalic acid). Dithionite-citrate (50 g L<sup>-1</sup> sodium dithionite in 0.35 M acetic acid/0.2 M sodium citrate) extraction was performed to extract amorphous and crystalline iron oxides. Deionized water alone was used to determine soluble iron content. Measurements were performed after 3, 5, 7, 14 and 25 days of stirring. After centrifugation, 50  $\mu$ L of supernatant was filtered, and then analyzed UV-visible spectrophotometer (*Varian Cary 50 Probe*) by 1,10, phenantroline method [24].

### 2.3. Experimental set-up

For preliminary tests, 2 g of PCP contaminated soil was transferred into glass vial of 40 ml and then mixed with oxidant solution. Final volume of reaction suspension was maintained at 2 ml to provide liquid/solid (L/S) ratio of 1:1. In experiments with magnetite or Fe<sup>0</sup>, nanoparticles were added and homogenized with the soil by magnetic stirring (400 rpm) before adding the oxidant. Blank tests were carried out without oxidants (with 2 mL of deionized water) and extracted concentration of PCP was considered as C<sub>0</sub>. The summary of experimental conditions is presented in Table 2.

Column experiments were conducted under water-unsaturated and water-saturated flow conditions (Fig. 1). The main characteristics of the columns are presented in Table 3. Column experiments under water-unsaturated conditions were conducted in glass columns of 160 mm length and 12 mm internal diameter. Columns were packed with 5 g of dry PCP-contaminated soil and sprinkled with oxidant solution with a help of peristaltic pump. The column was continuously weighted to check whether change in water content may occur during the flow experiment. A low flow rate (i.e. 0.025 mL min<sup>-1</sup>) was selected under water-unsaturated conditions, because it allowed keeping constant

water content of the column. The dose of injected oxidant and L/S ratio (i.e. injected volume to soil mass ratio) were varied (Table 4). Column experiments under water-saturated conditions were conducted in glass chromatographic columns of 185 mm length and 26 mm internal diameter. Columns were packed with 5 g of dry PCP-contaminated soil and wetted upward with deionized water to obtain saturated conditions. Porous volume was measured by weighting of column before and after water saturation. The dose of oxidants, L/S ratio and flow rate were varied (Table 4).

In open loop experiments (flow conditions I, II), oxidant solution was injected through the column and experiment was stopped when all oxidant solution was exhausted (i.e. around 67 h were necessary to inject 100 mL of oxidant solution at  $0.025 \text{ mL min}^{-1}$ ) (Fig. 1a, 1b). In closed loop columns (flow condition III), similar conditions were maintained (i.e. 100 mL, 67 h). However, the effluent was collected and re-injected continuously through the column at a higher flow rate (i.e.  $0.25 \text{ mL min}^{-1}$ ) (Fig. 1c). Blank experiments were conducted in the same way, using deionized water instead of oxidant solution. Summary of experimental conditions are presented in Table 4.

Breakthrough curves (BTC) of oxidant were also determined as a function of time. For this purpose, HP and PS concentrations were determined by iodometric titration, and PM concentrations by colorimetric titration [25,26]. All batch and column experiments were performed in triplicates and results were expressed as a mean value of three experiments and standard deviation of the triplicates was less than 5%. Experiments were performed without adjustment of pH at room temperature ( $20 \pm 2^\circ\text{C}$ ). pH values measured at different oxidant doses are presented in Figures S1, S2 (See Supplementary Material).

#### **2.4. Extraction and analysis**

Soil slurries were extracted with methanol/water solution (50/50, v/v) (L/S ratio: 2/1) in ultrasonic bath during 60 min. Obtained suspension was centrifuged for 10 min at 4000 rpm. Then 2 ml of supernatant solution was sampled, filtered through  $0.2 \mu\text{m}$  filter and analysed. The pH was adjusted

(if needed) to  $7.2\pm 0.2$  with NaOH (1M) solution before extraction. Extraction efficiency at pH=7.0-7.5 was found to be more than 95%. Effluents obtained from column experiments were filtered and analysed as well.

The PCP concentrations were quantified by high-performance liquid chromatography (HPLC) Waters 2695 equipped with XBridge C18 Column (250 mm  $\times$  4.6 mm), an UV detector at 254 nm and an integrator (injection volume: 50  $\mu$ L). A mixture of acetonitrile and water (both acidified with formic acid 0.1% v/v) was used as a mobile phase at a flow rate of 1 ml  $\text{min}^{-1}$ . Gradient mode was realised from 20/80 (acetonitrile/water, v/v) ramped to 80/20 in 12 min, hold 2 min and ramped back to 20/80. Extracts from soil and effluents were also analysed on Kinetex C18 reversed-phase column (100  $\times$  4.6 m; particles of 2.6  $\mu$ m) in order to identify formed carboxylic acids. The mobile phase consisted of deionized water adjusted to a pH of 2.7 by  $\text{H}_3\text{PO}_4$  and was pumped at a flow rate of 0.4 ml  $\text{min}^{-1}$ .

### 3. Results and discussion

#### 3.1. Preliminary oxidation tests

Preliminary oxidation tests were carried out in order to determine the optimal conditions for removal of PCP in the aged soil. First, experiments were performed in the absence and presence of magnetite and  $\text{Fe}^0$  nanoparticles, without pH adjustment (i.e. pH  $7.2\pm 0.1$ ) for HP and PS (Fig.S3). Magnetite and  $\text{Fe}^0$  nanoparticles were used because they are known to activate oxidant decomposition at circumneutral pH [27,28]. The PCP degradation with HP was found negligible with or without Fe-solids (Fig. S3), suggesting that the added catalysts were not able to activate HP at circumneutral pH and/or the radical formation was not strong enough to trigger PCP removal in soil. However, significant PCP removal (e.g. 12% (0.1 M of HP) and 36 % (1 M of HP)) was achieved when dissolved  $\text{Fe}^{2+}$  (0.08 mM) was used instead of Fe-solids for HP activation (pH of soil

suspension was decreased to 5.0), thereby underscoring the inability of Fe solids to promote Fenton reaction and remove PCP in soil under our experimental conditions.

In case of PS, similar amount of PCP (~ 50 %) was removed with or without addition of Fe-solids (Fig. S3). This may suggest that (i) PS may act without activation (i.e. electron transfer), (ii) added catalysts were not efficient to activate PS, and/or (iii) PS is already activated by soil constituents and further addition of new activators (e.g. synthetic Fe-solids) does not provide further improvement under our experimental conditions. To check the latter hypothesis, speciation of endogenous iron in soil was investigated by both chemical extractions and XRD. Firstly, no water dissolved iron was found. Oxalate and DCB extractions suggested that 40% of total iron in soil may be represented by amorphous iron oxides and only 3% by crystalline iron. However, the proportion of crystalline iron must be probably much higher, since DCB solution does not fully extract crystallized iron oxides, iron silicates or siderite [30,31]. XRD showed the presence of quartz and magnetite/maghemite in soil, as the main diffraction pics of  $\text{Fe}_3\text{O}_4$  were identified at  $30,1^\circ$  and  $35,5^\circ$   $2\theta$  (see Fig. S4). Although soil contains Fe-oxides that could activate oxidants, the data on hand cannot entirely rule out the direct oxidation mechanism of PS (i.e. electron transfer).

The effect of increasing oxidant dose was then evaluated for the three oxidants (Fig. 2). The HP showed the lowest degradation extent, which increased from 3 to 30% when concentration increased from 0.1 to 2 mol  $\text{L}^{-1}$ . PM has eliminated up to 67% of PCP at 200 mmol  $\text{L}^{-1}$ , and PS showed the highest efficiency with degradation extent reached 88% at 180 mmol  $\text{L}^{-1}$  of PS (Fig. 2).

The HPLC analysis has detected carboxylic acids, such as oxalic, glyoxalic, acetic, formic and maleic acids, confirming the oxidative degradation of PCP in the three oxidation systems. This could partially explain the pH fall of soil suspension (from 7 to around 5, see Fig. S1), observed in case of the highest PS concentration (Fig. S1). In addition, the initial pH of PS solutions was lower than that of other oxidants (HP and PM).

The PCP removal extent increased linearly when HP concentration increased from 0.1 to 1.5 M, and reached a plateau at 2 M, probably due to the scavenging of hydroxyl radicals by  $\text{H}_2\text{O}_2$  at high concentrations [9,27]. An exponentially-decaying dependence of percentage removal with increasing oxidant dose was also observed for PS and PM (Fig. 2). This behavior may result from scavenging effects expected at high oxidant doses and/or existence of different availability levels of PCP in soil. Indeed, removal efficiency increases with increasing oxidant dose and exponentially approaches a plateau as the residual PCP in soil is supposed to be less available and therefore less degradable. For PM,  $\text{MnO}_2$  formed at circumneutral pH may react with permanganate ions, resulting in non-productive consumption of oxidant [12, 29].

To overcome the non-productive consumption of oxidants at high oxidant doses, sequential addition of oxidant was tested and compared with single addition of the same oxidant dose (Fig. 3). For HP, no significant difference in removal extents was observed, probably due to its fast decomposition in the soil whatever the used concentration. In the case of PS and PM, sequential addition provided only improvement at high oxidant concentrations. Because of the slow decomposition of PS and PM in the soil [12, 29], more unproductive reactions may be expected at high oxidant doses, and therefore sequential addition of low oxidant doses should be preferred over the single addition of a high amount.

### ***3.2. PCP oxidation under flow-through conditions***

Column experiments were conducted according to conditions presented in Table 4 (flow conditions I, II). One column was flushed with deionized water and served as a blank ( $C_0$ ).  $C_0$  was determined as a sum of PCP found in effluent and soil. Total PCP concentration extracted at the end of experiment corresponds to the sum of PCP extracted from the soil and PCP found in effluent. Oxidant doses for column experiments were chosen according to preliminary experiments results

(section 3.1). As the addition of activators did not improve the oxidation performance for HP or PS (See section 3.1.), oxidants were used alone in column experiments.

It should be noted that no attempt has been made to fix the initial pH of injected oxidant solutions. Due to the buffering capacity of soil, the final pH of effluents was slightly higher than the pH of respective injected oxidant solutions in case of HP and PS. For PM, the injected solutions have a pH value close to that of soil (7.2), and so no significant pH variation was observed (Fig. S2).

**Water-unsaturated conditions.** All column experiments under water-unsaturated conditions were conducted at a constant flow rate of  $0.025 \text{ mL min}^{-1}$ , and water content is checked along the experiment. Obtained results indicated that oxidation efficiency followed the order  $\text{PM} > \text{PS} > \text{HP}$  (Fig. 4). For HP, increase in oxidant dose did not change significantly the total degradation extent (Fig. 4). A higher concentration of HP could not be used due to  $\text{O}_2$  release and column clogging up. The total degradation extent increased from 24 to 46% for PS and from 22 to 60% for PM when oxidant quantity increased from 0.1 to 1 mmol (Fig. 4), while further increase up to 2 mmol did not enhance the oxidation efficiency.

The mobility of PCP in soil is highly depended on pH of soil suspension, since the PCP aqueous solubility strongly increases with pH increasing [37, 38]. The increase in oxidant concentration slightly decreased the pH of injected solution and consequently that of soil effluent (from 7.1 to 6.8 for HP and from 6.6 to 4.1 for PS), whereas the increase in PM concentration increased the pH (from 7.2 to 7.6) of oxidant solution (Fig. S2). This pH variation in soil may explain why the PCP concentration in soil slightly increased with oxidant dose increasing for HP and PS, but decreased in case of PM (Fig. 4). Overall, increasing in oxidant dose mainly improved the degradation of PCP mobilized in the column effluent.

In further experiments, L/S ratio was changed by varying of the volume of injected solution (10-100 mL), while maintaining the same dose of oxidant (1 mmol) and soil mass in column (5 g). As more

PCP solubilisation is expected in a higher water volume, more PCP leaching/mobilization was observed at high L/S ratio (Fig. 5). This may explain the decrease in residual PCP concentration in soil with L/S ratio increasing observed in case of HP. For PS and PM, no significant effect of L/S ratio on the residual PCP concentration was observed (see the values with error bars in Fig. 5). Surprisingly, the total degradation extent slightly increased with L/S ratio decreasing: from 45 to 54%, from 51 to 60% and from 26 to 32% using PS, PM and HP respectively (Fig. 5). These results suggest that an injected solution with low oxidant concentration (or high water volume) (i.e. high L/S) may increase the mobility and transport of contaminants, but with no further degradation. Overall, PCP degradation extents under water-unsaturated conditions did not exceed 60%. In fact, presence of gas phase and/or preferential pathways in column resulting from unsaturated conditions (water flow is only due to gravity gradient) may be not in favor for an optimal contact between oxidant and contamination zones. To check this hypothesis, further experiments were conducted under water-saturated conditions.

**Water-saturated conditions.** The first experiments conducted at a flow rate of  $0.025 \text{ mL min}^{-1}$ , as in water-unsaturated conditions showed the same order of oxidation efficiency, *i.e.*  $\text{PM} > \text{PS} > \text{HP}$ . The total degradation extent using HP did not changed significantly (26-30%) when oxidant dose increased from 1 to 5 mmol (Fig. 6). As under water-unsaturated conditions, the mobilized part of PCP using PS and PM decayed with oxidant dose increasing, resulting in higher total degradation extent (Fig. 6). As for previous experiments, the increase in oxidant dose led to a slight pH variation in soil, which may explain the variation in PCP concentration in soil with oxidant dose increasing. Overall, increasing in oxidant dose improved the degradation of PCP mobilized in the case of PS and PM.

No significant effect of L/S ratio was observed in the case of HP (28-29%) and PS (51-54%), except for PM where oxidation efficiency increased (from 27 to 41%) with L/S ratio decreasing (Fig. 7).

As for water-unsaturated conditions, the residual PCP concentration in soil decreased with L/S ratio for HP while very small effect was observed for PS and PM (see the values with error bars in Fig. 7). Collectively, these results indicate that the water content (water-unsaturated vs. water-saturated) do not significantly influence the oxidation performance in the PCP-contaminated soil.

In order to evaluate the impact of residence time on oxidation efficiency of PCP, different flow rates ( $0.025$  to  $2.5 \text{ mL min}^{-1}$ ) were tested under water-saturated conditions (Fig. 8). No significant change in overall degradation extent was observed for HP, which can be explained by its high reactivity and rapid decomposition [12]. Degradation extents decreased for PS (54 to 39%) and PM (33 to 26%) with increasing flow rate, suggesting the lack of local equilibrium in column (more pronounced in case of PS). The impact of kinetic limitations in column is usually evaluated by determining Damköhler number (Da) that relates the ratio of hydrodynamic residence time to characteristic time for chemical reaction in the column [32,33]. Unfortunately, the lack of kinetic data of PCP in soil (oxidation efficiency was evaluated only at the end of experiment) and mass transfer rate in column does not allow the estimation of Da number [34]. Nevertheless, the present findings showed clearly that kinetic limitations affect the oxidation extent in column (particularly for PS), and a lower flow rate ( $0.025 \text{ mL min}^{-1}$ ) is likely preferred for efficient degradation.

***Oxidant decomposition.*** Breakthrough curves (BTC) of oxidant were determined at two L/S ratios (or two different injected volumes) under water-saturated conditions, and are presented in Figure 9. Only traces of HP were found in effluent when high volume of oxidant (1 mmol in 100 mL) was injected, corroborating the rapid decomposition of HP in soil (Fig. 9). When injected volume was decreased 10 times (i.e. 1 mmol in 10 mL), oxidant ( $C/C_0 = 0.4$ ) was flushed out of the column at  $V_p$  (Pore Volume) = 6. In both tested conditions, PS breaks out very early, i.e. at one  $V_p$ , and reached complete breakthrough at 20  $V_p$  at lower inflow concentration and 2  $V_p$  at higher inflow concentration (Fig. 9), suggesting that PS decomposition in soil is relatively low. Outflow

concentrations of PM gradually increased with time, and a long tailing was observed before reaching complete breakthrough at the end of experiment. Similar BTC and overall oxidant decomposition ( $\pm 5\%$ ) were obtained in water-unsaturated conditions (not shown), further confirming that the water content in column (water-unsaturated vs water-saturated) has no significant impact on the oxidation process under our experimental conditions.

For all oxidant systems, increasing in flow rate from 0.025 to 2.5 mL min<sup>-1</sup> decreased the oxidant decomposition (data not shown), thereby confirming the kinetic limitations occurred due to the short residence time of oxidants. Collectively, these results suggest that oxidants and particularly PS and PM were not completely consumed even when a low flow rate was applied. In order to optimize the consumption of oxidants in soil column, effluent was collected and then re-injected in a closed-loop recirculating system.

### **3.3. Closed-loop recirculation of oxidant**

Column experiments were conducted according to conditions presented in a closed-loop recirculating system (Table 4). The same oxidant dose (1 mmol) and water volume (100 mL) was used for HP, PS and PM (total time 67h at 0.25 ml min<sup>-1</sup>). In these conditions, 62%, 70% and 27% of PCP were degraded in presence of PS, PM and HP respectively (first column in each graph in Fig. 10). As HP is rapidly decomposed, recirculation did not enhance the removal extent of PCP. Only the part of mobilized PCP increased in the closed-loop recirculating system (35% vs. 27% in open loop). However, recirculation of oxidant solution improved the oxidation efficiency in case of PS and PM (62% vs. 52% and 70% vs. 53%). This is corroborated by the measurements of oxidant concentration in the closed-loop reactor after 67 h of recirculation. Indeed, the oxidant decomposition extent increased from 5 to 13% for PS and from 28 to 36% for PM.

Higher oxidant doses (i.e. 5 mmol for HP and 2 mmol for PS or PM) improved PCP removal extents, i.e. from 28 to 41% for HP and from 62 to 73% for PS, while for PM the degradation extent

stayed almost constant (~73%). As for previous experiments, the addition of Fe-solids did not improve the oxidation efficiency for HP or PS in the closed-loop recirculating system.

It is generally accepted that degradation of organic contaminants can be limited by their low availability in soil, and addition of solubility-enhancement agents may improve degradation extents [35,36]. In order to enhance the availability of PCP in soil, experiments were carried out using methyl- $\beta$ -cyclodextrin (M- $\beta$ -CD). This non-toxic and biodegradable cyclodextrin derivative was selected because it is known to enhance the aqueous solubility of PCP [36,37]. Column tests conducted by injecting M- $\beta$ -CD solution (25 mM) showed that PCP mobilization increased significantly, *i.e.* 61% of mobilized PCP *vs.* 37% with only water. However, the presence of M- $\beta$ -CD in oxidation experiments did not enhance the PCP removal extent (Fig. 10). Only the mobilized PCP concentration increased in the HP case when M- $\beta$ -CD was used. It should be noted that cyclodextrin derivatives may scavenge radicals and thus compete with target contaminants for oxidation reaction [38].

In order to overcome this issue and thus enhance the PCP solubility/availability without addition of chemical agents, column experiments were conducted at 40 °C. It is known that the thermal pre-treatment may enhance the availability of organic compounds in contaminated soils where pollutant availability is a limiting factor [39]. Surprisingly, no improve in PCP degradation extents were observed for PM and PS at 40°C (Fig. 10), though heating is known to effectively activate PS [40]. As a matter of fact, PS concentrations in the closed-loop reactor decreased at 40°C, whereas heating did not affect PM decomposition (Fig. 11). This may suggest that PCP is primarily degraded via electron transfer with PS, and activation of PS to generate radicals (thermally or chemically by using iron species) did not provide any improvement in removal extents.

In case of HP, the total oxidation extent has significantly increased (53% *vs.* 27%), but only the part of mobilized PCP has been diminished. The increase of temperature can enhance the compound

solubility, but also accelerate the formation of  $\text{OH}^\bullet$  radicals and, therefore, degradation extents as previously reported [41].

It is worth noting that the presence of M- $\beta$ -CD affects only the decomposition of HP, and not PS or PM (Fig. 11). It is previously reported that the presence of inorganic ligands such as silicates, phosphates may decrease the decomposition rate of HP through sorption to surface active sites in heterogeneous Fenton process [27,42]. By analogy, M- $\beta$ -CD as an organic ligand may sorb to soil constituents and thus blocking catalytical sites for HP decomposition. In contrast to previous reports where decrease in removal extent of organic compounds often accompanies decrease in HP decomposition rate [43,44], no change in removal extent of PCP was observed in the present study. Higher concentrations of M- $\beta$ -CD have significantly limited the decomposition of HP and so increased the lifetime of HP in reaction medium (Fig. 12). Indeed, the HP concentrations in the closed-loop reactor were positively correlated with M- $\beta$ -CD concentration, and reached zero at the end of experiments (*i.e.* 67 h) whatever the M- $\beta$ -CD concentration.

#### 4. Conclusions

In this study, we have notably demonstrated that PCP can be effectively removed from contaminated soil by using hydrogen peroxide, permanganate and persulfate and under both water-unsaturated and water-saturated conditions. HP and PS act without activation and the addition of iron-based catalysts at circumneutral pH did not improve the oxidation efficiency. The results of PCP removal extent and oxidant decomposition indicated that the water content in column (water-unsaturated vs water-saturated) has no significant impact on the oxidation performance under our experimental conditions. Only, the mobilized part of PCP using PS and PM decayed with oxidant dose increasing, resulting in higher total degradation extents. More PCP mobilization was observed at high L/S ratio or when a high water volume was used, but no significant effect of L/S ratio on the overall oxidation extent was detected. Decreasing in residence time of oxidant affected the oxidant

decomposition as well as PCP degradation extent, thereby underscoring kinetic limitations in column. Consistently, recirculation of oxidant solution improved the oxidation efficiency and oxidant decomposition extents in case of PS and PM, but not for HP where only the part of mobilized PCP increased in the closed-loop recirculating system. Surprisingly, attempts to enhance the PCP availability in soil by using solubility agents or by heating did not improve the degradation efficiency in soil. The inability of temperature as well Fe species to enhance the PCP degradation in case of PS may suggest that PCP is mainly degraded via electron transfer with PS. The presence of M- $\beta$ -CD affects only the decomposition of HP, which is positively correlated with the M- $\beta$ -CD concentration. Higher persistence of HP could be advantageous for *in situ* chemical oxidation where delivery of oxidant to zone-source of contamination can be limited by the high reactivity (or the low lifetime) of oxidants. Collectively, these results may have strong implications in the application of chemical oxidation under flow-through conditions closer to field conditions.

### **Acknowledgments**

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## Tables

**Table 1.** Physical and chemical characteristics of sampled soil.

Parameter	Value	Unit
<i>Soil texture</i>		
Silt	12.4	wt%
Clay	0.6	wt%
Sand	87.0	wt%
pH (in water)	7.2	
Cation exchange capacity	4.0	meq/100
Soil organic matter (SOM)	1.5	wt%
Calcium carbonate (CaCO <sub>3</sub> )	0.3	wt%
<i>Exchangeable cations</i>		
Exchangeable calcium (CaO)	1337	mg kg <sup>-1</sup>
Exchangeable magnesium (MgO)	36	mg kg <sup>-1</sup>
Exchangeable potassium (K <sub>2</sub> O)	64	mg kg <sup>-1</sup>
Available phosphorus (P <sub>2</sub> O <sub>5</sub> )	8	mg kg <sup>-1</sup>
<i>Metals</i>		
Cadmium (Cd)	<0.5	mg kg <sup>-1</sup>
Chromium (Cr)	13.4	mg kg <sup>-1</sup>
Total copper (Cu)	19	mg kg <sup>-1</sup>
Nickel (Ni)	2.2	mg kg <sup>-1</sup>
Lead (Pb)	5	mg kg <sup>-1</sup>
Total Zinc (Zn)	39	mg kg <sup>-1</sup>
Mercury (Hg)	0.25	mg kg <sup>-1</sup>
Total Iron (Fe)	9759	mg kg <sup>-1</sup>

**Table 2.** Summary of batch experimental conditions.

Oxidant	Oxidant quantity, mmol	Activator, [Fe]: 5 mg g <sup>-1</sup>	Volume of water, ml	L/S ratio	Duration, h
Blank	-	-	2	1/1	72, 120
HP	0.2-4 (single)	None, Fe <sub>3</sub> O <sub>4</sub> , Fe <sup>0</sup>	2	1/1	72
	2-4 (sequential)				120
PS	0.002-0.36*	None, Fe <sub>3</sub> O <sub>4</sub> , Fe <sup>0</sup> ,	2	1/1	72
	0.01-0.2 added in 5/10 times				120
PM	0.002-0.4	None	2	1/1	72
	0.01-0.2 added in 5/10 times				120

\* Maximum tested K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration, limited by its low solubility

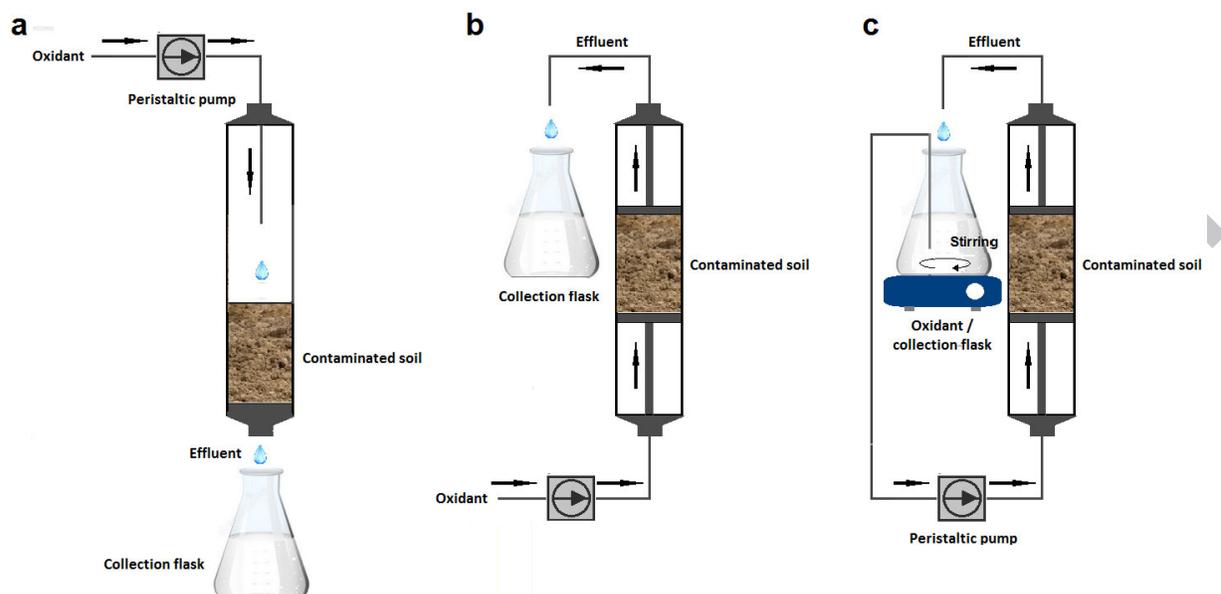
**Table 3.** Summary of column characteristics.

	Flow condition I (unsaturated, open loop)	Flow condition II (saturated conditions, open loop)	Flow condition III (saturated conditions, closed loop)
Soil weight, g	5	5	5
Column section, cm <sup>2</sup>	1.06	5.3	5.3
Height of bed, cm	4.0	0.8	0.8
Bed density ρ*, g cm <sup>3</sup>	1.19±0.01	1.2±0.01	1.2±0.01
Pore volume V <sub>p</sub> , mL	1.31	1.73	1.73
Flow rate, ml min <sup>-1</sup>	0.025	0.025; 0.25; 2.5	0.25
Porosity, θ	0.31	0.41	0.41
Q, cm min <sup>-1</sup>	0.024	0.005; 0.05; 0.5	0.05
Velocity, cm min <sup>-1</sup>	0.077	0.012; 0.12; 1.2	0.12

\*Uniform bulk density of dry porous bed of soil

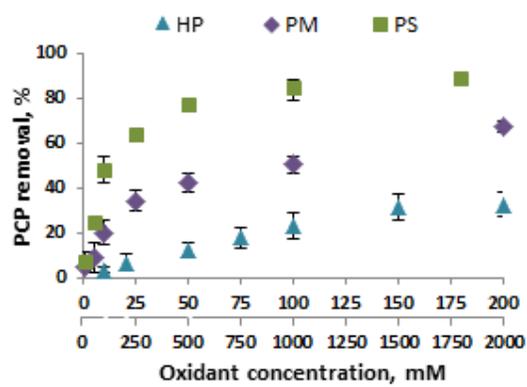
**Table 4.** Summary of column experimental conditions.

Oxidant	Oxidant concentration, mM	Volume of water, ml	L/S ratio	Other conditions	Flow rate, mL min <sup>-1</sup>	Flow conditions	
Blank	-	100	20/1	-	0.025	I, II, III	
	-	100	20/1	M-β-CD: 25 mM	0.025	I, II, III	
HP	1, 2, 5	100	20/1	-	0.025	I, II	
	1	50	10/1	-	0.025	I, II	
	1	10	2/1	-	0.025	I, II	
	1	100	20/1	-	0.25, 2.5	II	
	1, 5	100×10	20/1	-	0.25	III	
	1	100×10	20/1	M-β-CD: 1, 5, 25 mM	0.25	III	
	1	100×10	20/1	40 °C	0.25	III	
	1	100×10	20/1	Fe <sub>3</sub> O <sub>4</sub> , Fe <sup>0</sup> : 5 mg g <sup>-1</sup>	0.25	III	
	PS	0.1, 1, 2	100	20/1	-	0.025	I, II
		1	50	10/1	-	0.025	I, II
1		10	2/1	-	0.025	I, II	
1		100	20/1	-	0.25, 2.5	II	
1, 2		100×10	20/1	-	0.25	III	
1		100×10	20/1	M-β-CD: 25 mM	0.25	III	
1		100×10	20/1	40 °C	0.25	III	
1		100×10	20/1	Fe <sub>3</sub> O <sub>4</sub> , Fe <sup>0</sup> : 5 mg g <sup>-1</sup>	0.25	III	
PM		0.1, 1, 2	100	20/1	-	0.025	I, II
		0.1, 1	50	10/1	-	0.025	I, II
	0.1, 1	10	2/1	-	0.025	I, II	
	0.1	100	20/1	-	0.25, 2.5	II	
	1, 2	100×10	20/1	-	0.25	III	
	1	100×10	20/1	M-β-CD: 25 mM	0.25	III	
	1	100×10	20/1	40 °C	0.25	III	

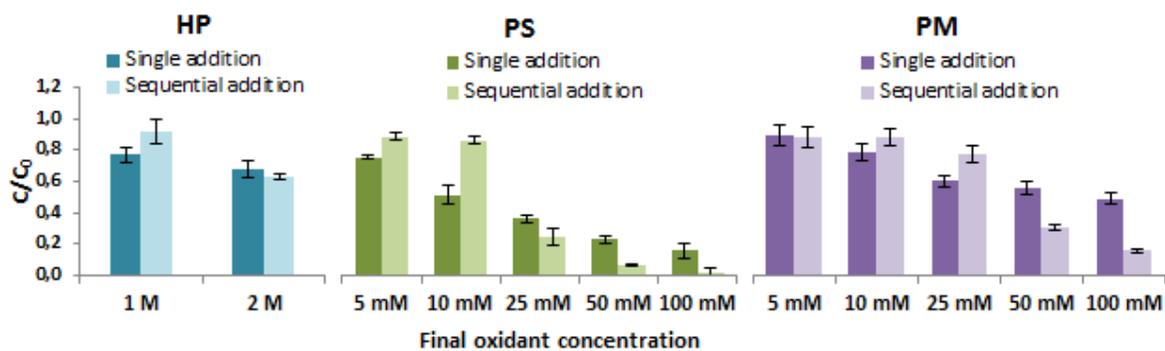


**Fig. 1.** Scheme of column experimental set-up: a) water-unsaturated conditions/open loop, b) water-saturated conditions/open loop and c) water-saturated/closed loop.

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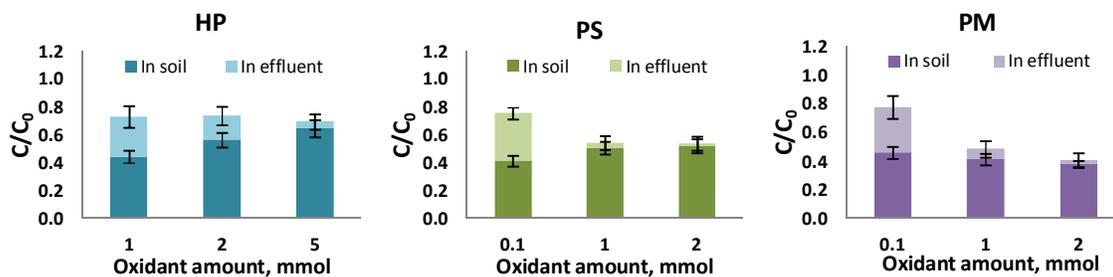


**Fig. 2.** PCP concentration in soil after chemical oxidation in batch:  $[\text{H}_2\text{O}_2] = 100\text{-}2000$  mM;  $[\text{PS}] = 1\text{-}180$  mM;  $[\text{PM}] = 1\text{-}200$  mM; L/S ratio = 1/1.

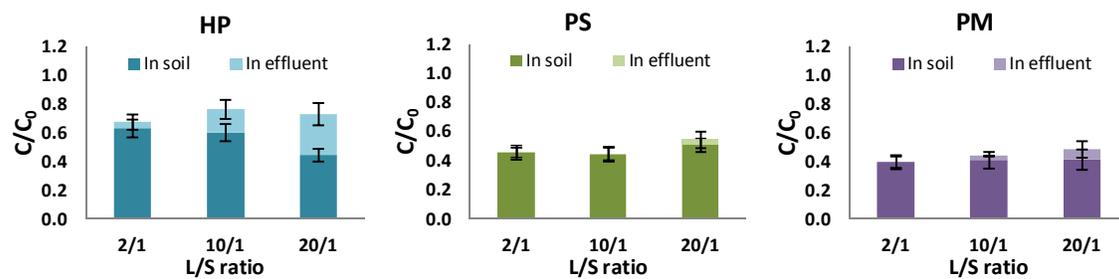


**Fig. 3.** PCP concentration in soil after chemical oxidation in batch: [HP] = 1 and 2 M (in sequential addition 10 and 20 mM x 10); [PS, PM] = 5,10, 25, 50 and 100 mM (0.5, 1, 2.5, 5 and 10 mM x 10). L/S ratio = 1/1.

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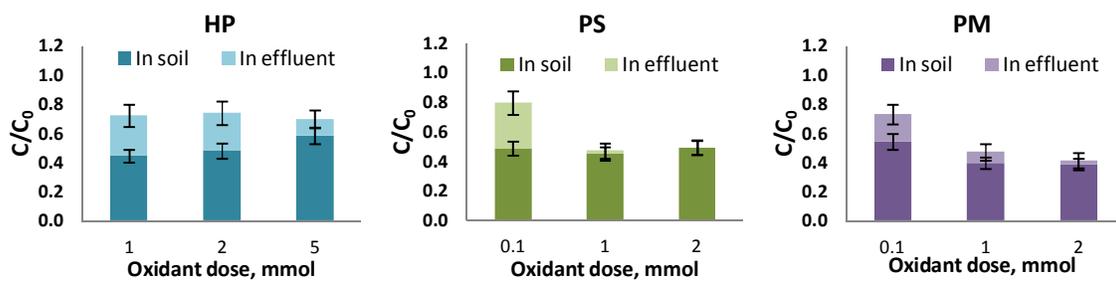
**Fig. 4.** PCP concentration in soil and effluents after chemical oxidation under water-saturated flow-through conditions (open loop): HP = 1, 2, 5 mmol; PS, PM = 0.1, 1, 2 mmol; L/S ratio = 20/1; Flow rate: 0.025 ml  $\text{min}^{-1}$ .



**Fig. 5.** PCP concentration in soil and effluents after chemical oxidation under water-unsaturated flow-through conditions (open loop). Oxidant dose: 1 mmol; L/S ratio = 2/1, 10/1, 20/1; Flow rate: 0.025 ml min<sup>-1</sup>

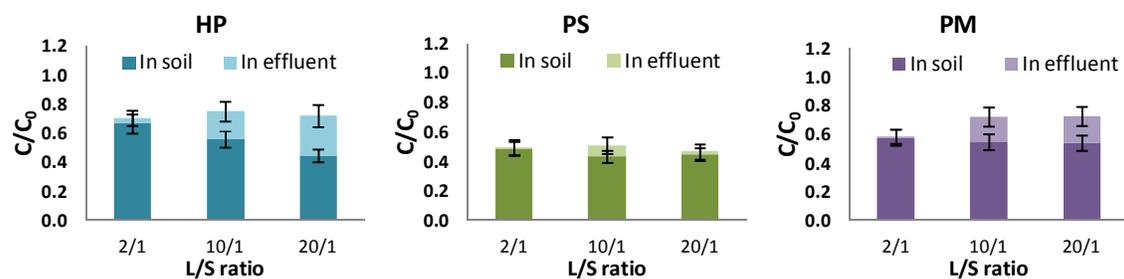
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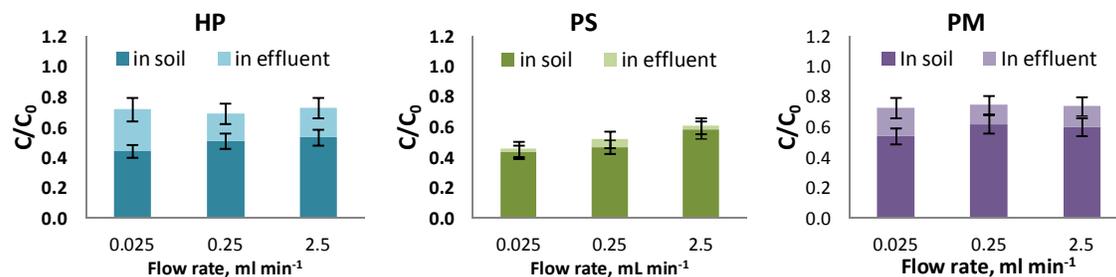
**Fig. 6.** PCP concentration in soil and effluents after chemical oxidation under water-saturated flow-through conditions (open loop): HP = 1, 2, 5 mmol; PS, PM = 0.1, 1, 2 mmol; L/S ratio = 20/1; Flow rate: 0.025 ml  $\text{min}^{-1}$ .

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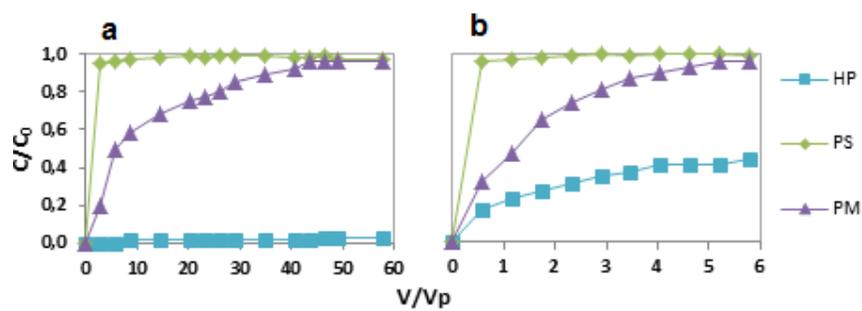
**Fig. 7.** PCP concentration in soil and effluents after chemical oxidation under water-saturated flow-through conditions (open loop): HP = 1 mmol; PS = 1 mmol; PM = 0.1 mmol; L/S ratio = 20/1, 10/1, 2/1; Flow rate: 0.025 ml min<sup>-1</sup>.

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**Fig. 8.** PCP concentration in soil and effluents after chemical oxidation under water saturated flow-through conditions (open loop): HP, PS = 1 mmol; PM = 0.1 mmol; L/S ratio = 20/1; Flow rate: 0.025, 0.25, 2.5  $\text{ml min}^{-1}$ .

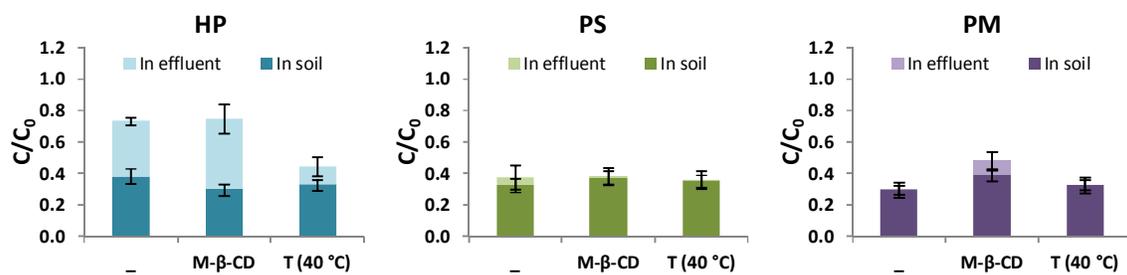
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**Fig. 9.** Breakthrough curves of oxidants: HP, PS, PM = 1 mmol; Flow rate = 0.025 ml min<sup>-1</sup>.

**a:** L/S ratio = 20/1 (i.e. injected volume 100 mL). **b:** L/S ratio = 2/1 (i.e. injected volume 10 mL).

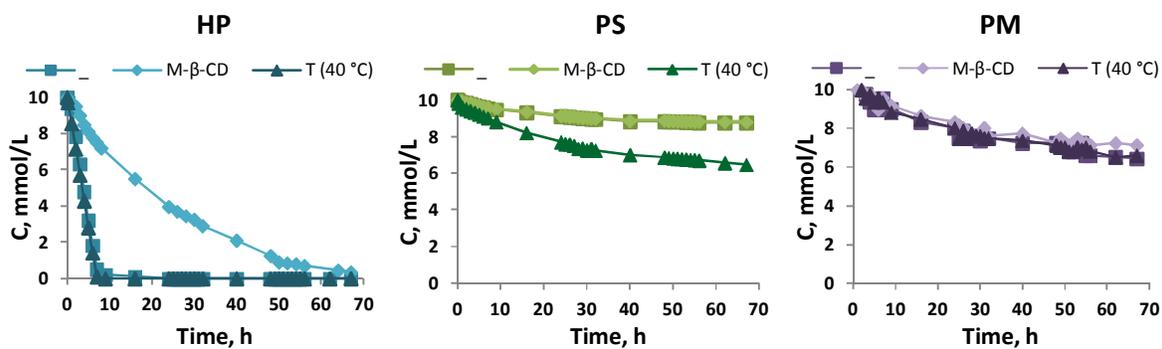
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**Fig. 10.** PCP oxidation extents under water-saturated flow-through conditions (closed loop): HP, PS, and PM

$= 1 \text{ mmol}$ ;  $[\text{M-}\beta\text{-CD}] = 0.25 \text{ mM}$ ;  $\text{L/S ratio} = 20/1$ ;  $\text{Flow rate} = 0.25 \text{ ml min}^{-1}$ .

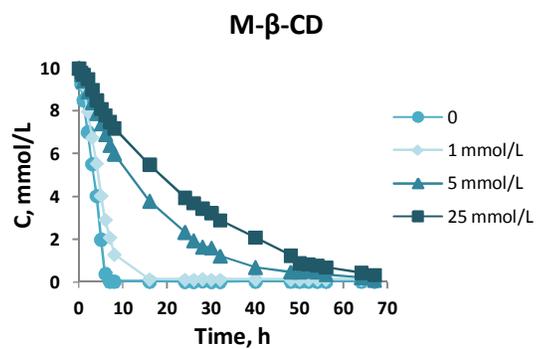
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**Fig. 11.** Evolution of oxidant concentrations under water-saturated flow-through conditions (closed loop):

[HP, PS, PM] = 1 mmol ( $C_0=10$  mM); L/S ratio = 20/1; Flow rate:  $0.25$  ml  $\text{min}^{-1}$ .

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**Fig. 12.** Evolution of HP concentration in presence of M- $\beta$ -CD under water-saturated flow-through conditions. HP = 1 mmol; [M- $\beta$ -CD] = 0, 1, 5, 25 mM, L/S ratio = 20/1; Flow rate: 0.25 ml min<sup>-1</sup>.

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*Highlights*

- PCP can be effectively removed from contaminated soil at circumneutral pH.
- Water content or porosity did not affect mobility or degradation of PCP in soil.
- Increasing in flow rate decreased oxidant decomposition and PCP degradation extents.
- Addition of cyclodextrin slowed down the decomposition rate of H<sub>2</sub>O<sub>2</sub>.
- Closed-loop recirculating system improved the PCP removal extent.

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