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Application of H_2O_2 lifetime as an indicator of TCE Fenton-like oxidation in soils

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Abstract

Hydrogen peroxide decomposition and trichloroethylene (TCE) oxidation kinetics were studied through batch slurry experiments, performed on two TCE contaminated soils (a sandy soil and a clay soil), characterized by different texture and organic fraction; besides, experiments were also performed on sandy soil columns, in order to more closely reproduce the typical conditions of an in situ treatment. The results of the batch tests indicated that hydrogen peroxide lifetime was correlated to the oxidation efficiency; namely, complete TCE oxidation was achieved only for the conditions characterized by longer hydrogen peroxide lifetime, that was obtained by addition of a proper stabilizer (KH_2PO_4). The soil properties were also observed to influence both hydrogen peroxide decomposition and TCE oxidation kinetics, probably as a consequence of the different TOC content. The soil column experiments, performed on 10, 20, and 30 cm long columns, indicated that hydrogen peroxide decomposition, which was almost complete at 30 cm depth, was on the contrary negligible when the stabilizer was added. In agreement with this observation, the performance of TCE oxidation were greatly improved in the latter case.

Based upon the collected results, it can be concluded that hydrogen peroxide experiments may be useful, at least in the first screening phase of the design activity, for selecting, among the different operating conditions, those that may be potentially more effective for the oxidation treatment.

Keywords: AOPs; TCE; Hydrogen peroxide; Fenton; Soil

1. Introduction

Remediation of sites contaminated with biorefractory pollutants, such as chlorinated aliphatics, halogenated phenols, and PAHs, represents a typical application for advanced oxidation processes (AOPs). A review of AOPs application to in situ chemical treatment of contaminated soils and groundwater was provided by Yin and Allen [1]. Their operational principle is based on the idea of generating a pool of oxidizing species in the subsurface environment. The different AOP processes differ simply in the way this pool is produced. For instance, potassium permanganate has been applied as oxidizing agent for the in situ chemical treatment of contaminated sites [2]; also ozone has been shown to readily oxidize organic compounds [3]. One of the more typical advanced oxidation process is based on the property of hydrogen peroxide to generate hydroxyl radicals by reacting with ferrous ions in the well known Fenton's reaction:

$$H_2O_2 + Fe^{++} \rightarrow Fe^{+++} + OH^{\bullet} + OH^{-}$$

The possibility of applying this process to contaminated soils was first demonstrated by Watts et al.[4] in batch lab-scale experiments and later by Ravikumar and Gurol [5] with sand-packed column tests and by Kakarla and Watts [6] with soil-packed column tests. Ho et al. [7] also developed an injection system for in situ catalyzed peroxide remediation of contaminated soils. In these works, the possibility of using the iron present in the soil as catalyst possibly without pH adjustment, the so-called Fenton-like process, was also investigated. The role played by the soil iron minerals in determining the oxidation efficiency was investigated by Watts et al. [8], adding goethite to the reaction environment. The obtained results demonstrated that one of the main drawbacks of an in situ Fenton-like treatment relies in the instability of hydrogen peroxide, when it gets in touch with

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inorganic compounds, such as iron oxyhydroxides and manganese oxyhydroxides catalysts or with organic compounds, such as catalase or peroxidase enzimes, that are widespread in surface soils [5]. This instability may dramatically reduce the concentration of hydrogen peroxide at increasing soil depths unless a proper stabilizer substance, such as a phosphate salt, is mixed with hydrogen peroxide [5,6]. The decomposition of hydrogen peroxide in subsurface environments was also studied, even if in model systems [9,10].

The selection of the more appropriate operating conditions for an in situ treatment, based on the Fenton's or Fenton-like process, is usually accomplished through lab-scale oxidation experiments, that require monitoring the concentration of the pollutant(s), with often time-expensive and cumbersome extraction/analytical procedures. Recently, Baciocchi et al. [11] proposed a simplified procedure based on the use of hydrogen peroxide lifetime as a readily measurable indicator of the oxidation efficiency of Fenton's and Fenton-like systems. This procedure greatly simplifies at least the first screening phase of the operating conditions, allowing to reduce the number of cases to be tested completely. The validity of this approach was demonstrated in slurry phase experiments performed on 3-chlorophenol contaminated soils.

In this work hydrogen peroxide lifetime was used as indicator of the oxidation efficiency of Fenton-like processes applied to two different soils contaminated with trichloroethylene (TCE). A reactivity scale, in terms of the oxidizing power in two different operating conditions (H_2O_2 alone, H_2O_2 amended with a stabilizer) was built as a function of the hydrogen peroxide lifetime. Its validity was then assessed through TCE Fenton-like oxidation experiments performed both in slurry phase and in soil columns.

2. Materials and methods

2.1. Reagents

Hydrogen peroxide (30%), iron (Fe II) sulfate, methanol, and ethanol (HPLC grade) used for standard mixtures preparation, sulfuric acid (96%), potassium monobasic phosphate, and hydrochloric acid (37%) were all purchased from Carlo Erba (Milan, Italy). Trichloroethylene (TCE, 99% pure) was purchased by Fluka (Germany).

2.2. Characterization of soil samples

The soils selected for the present study were collected in two different areas located near Rome. Namely, soil 1 was a surface soil collected near the Tevere river in Rome, whereas soil 2 was collected in S. Policarpo (Rome). Preliminary extraction tests indicated that phenols concentration in both soil types was below the detection limit. The total organic carbon measured following the Walkey–Black procedure [12], was 0.11% for soil 1, whereas it was 0.90% for soil 2. Both soils were air dried and passed through a 2 mm sieve. The particle size distribution of the soil fractions below 2 mm, not reported for sake of conciseness, clearly indicated that soil 1 is characterized by a much higher clay content than soil 1. Therefore, soil 1 was classified as a sand, whereas soil 2 as a clay sand with loam. Iron and manganese concentrations in different chemical forms, determined by selective extraction following the Tessier method [13] and measuring the selective leachate with a 3030 B spectrophotometer (Perkin Elmer, Norwalk CT), are reported in Table 1. Both iron and manganese oxides, that are considered among the most active catalysts of hydrogen peroxide decomposition in soils [10], were found to be about one order of magnitude larger in soil 2 than in soil 1.

2.3. Batch hydrogen peroxide decomposition tests

Kinetics of hydrogen peroxide degradation were studied through batch experiments, performed in 50 ml amber glass vials, kept in continuous agitation (6.7 Hz) on a multiposition magnetic stirrer, supplied by VELP scientifica (Italy). The temperature was not controlled, but was continuously monitored during the experiment and remained always in the $22 \pm 1\,^{\circ}C$ range. A 2.5 g soil sample was added to the vial, together with 12 ml of distilled water. Monobasic potassium phosphate could be eventually added to the soil slurry. The initial pH of the soil slurry was measured with a portable pH meter HI 8314 (Hanna Instruments). The experiment was then started adding hydrogen peroxide to the soil slurry in the desired quantity, as described in the following section. The reaction was stopped adding few drops of hydrochloric acid to the sample immediately after its collection from the soil slurry [4]. Then, a sample of the slurry was collected and immediately centrifuged at 67 Hz for 15 min in a PK 110 centrifuge supplied by ALC (Italy). After centrifugation, the supernatant was analyzed for hydrogen peroxide, as described below. Repeating the same batch experiment by sampling at different reaction times allowed to obtain the kinetics of hydrogen peroxide decomposition.

2.4. Batch TCE degradation tests

The TCE contaminated solution was prepared in 250 ml serum bottles (Supelco), completely filled with distilled water, by injecting a given amount of pure TCE through the bottles septa. TCE was dissolved by stirring the solution for 24 h on a multiposition magnetic stirrer, supplied by VELP scientifica (Italy). A 3.0 g soil sample was placed in a 15 ml glass vial (Supelco) and it was contaminated by injecting 15 ml of the TCE solution through the vial septum and stirring the soil slurry for 3 h, until adsorption equilibrium was achieved. The resulting TCE concentration was 1000 ± 50 mg/kg. TCE oxidation experiment was started by replacing the liquid supernatant with the same volume of a solution with hydrogen peroxide and other components, such as hydrogen chloride, stabilizer, iron sulfate, when required. TCE oxidation was stopped by adding few drops of

Table 1
Distribution of the different iron and manganese fractions (according to Tessier differentiation) in soil 1 and soil 2

	Soil 1		Soil 2	
	Fe (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
Easily exchangeable	4.06	3.12	0.96	2.56
Bound to carbonates	170	110	2.16	2.72
Bound to oxides	1070	170	8634	1051
Bound to organic matter or as sulfides	33	1.3	76.5	15.5
Residual fraction	14757	2833	19450	276
Total	16030	3120	28160	1348

hydrogen chloride. For each operating condition to be studied, several vials were prepared and in each one the reaction was stopped at different times; the TCE residual concentration in each vial was then determined allowing to obtain from these data the TCE oxidation kinetics.

2.5. Column tests

The experimental set-up consisted in Plexiglass™ columns, with a 10, 20 or 30 cm height and an internal diameter of 2.5 cm. Hydrogen peroxide decomposition tests were performed by feeding from top to bottom an hydrogen peroxide solution through the soil column, the concentration of hydrogen peroxide was monitored by collecting liquid samples at the column outlet.

TCE oxidation experiments were performed as follows. A 500 mg/l TCE solution in distilled water was prepared in 5 l Pyrex bottles by mixing pure TCE and distilled water for 24 h. The obtained TCE solution, transferred to a 10 l tedlar bag (SKC), was fed from top to bottom of the column by a peristaltic pump (VELP scientifica) in order to contaminate the soil. After a 24 h equilibration time, liquid samples were collected at the sampling ports and analyzed for TCE. The difference between actual and inlet TCE concentration was used to calculate the TCE amount adsorbed on soil. Then, the resulting contaminated soil (TCE concentration 1000 ± 100 mg/kg) was treated with an hydrogen peroxide solution (with or without stabilizer) and the treatment efficiency evaluated with respect to a desorption treatment performed feeding water alone. The flow rate was always 4.5 ml/min again from top to bottom.

2.6. Analytical methods

Determination of TCE in soil and supernatant was obtained by the SPME technique coupled to gas chromatography-flame ionization detection (GC-FID). The SPME extractions were done using a manual 65 μm DVB-PDMS SPME device purchased from Supelco (Bellefonte, PA, USA). The SPME content was then analyzed by means of GC-FID using an Autosystem XL gas chromatograph (Perkin-Elmer, Norwalk, CT) equipped with a 30 m × 0.25 μm i.d. SPB5 capillary column (Supelco).

Determination of hydrogen peroxide was performed by the iodometric method [14].

3. Results and discussion

3.1. Batch tests

The results of H_2O_2 decomposition kinetics performed in two different operating conditions for each soil type are summarized in Table 2. The collected data were fitted with a first-order model, in agreement with previous works [11]. The corresponding kinetic constants, reported in Table 2 together with the H_2O_2 lifetimes, clearly indicated that the operating conditions may dramatically affect the H_2O_2 decomposition. As far as soil 1 is concerned, when hydrogen peroxide only was applied (case B in Table 2a), its decomposition was observed to be fast, with a 440 min lifetime. A much higher H_2O_2 lifetime (9210 min) was observed when a stabilizer was used (case A in Table 2a). The same operating conditions were tested for soil 2, showing the same behavior even if with different experimental results. Namely, as shown in Table 2b, the lifetime in the presence of H_2O_2 only was equal to 8 min and was increased to 1150 min by addition of a stabilizer. The different hydrogen peroxide decomposition observed between the two soils may be explained with the different content in manganese and iron oxides (higher for soil 2) that are responsible of the "non-productive" H_2O_2 decomposition pathways, such as the disproportion to O_2 and H_2O. Also the different texture of the two soils, as well as the different TOC content, may have played an important role, since the smaller particles present in the clay fraction (present only in soil 2) may act as an effective catalyst of H_2O_2 decomposition.

Based upon the H_2O_2 decomposition data, it was possible to rank the two tested operating conditions in terms of the expected Fenton-like oxidation efficiency. Namely, for each soil type, the operating conditions with longer H_2O_2 lifetimes (i.e. smaller H_2O_2 decomposition kinetic constant) should correspond to higher oxidation efficiencies.

The validity of this scale was tested by performing slurry phase TCE oxidation experiments on soil 1 and soil 2. The results are summarized again in Table 2 in two forms: resid-

Table 2
Hydrogen peroxide decomposition and TCE oxidation batch tests: operating conditions (pH and stabilizer concentration) for both experiments

Operating case	pH	Stabilizer (mM)	Kinetic constant (min^{-1})	H_2O_2 lifetime (min)	TCE residual concentration ($mg\,kg^{-1}$)	TCE degradation yield ($mg\,kg^{-1}\,min^{-1}$)
(a)						
A	6.5	25.9	5×10^{-4}	9210	0.3	0.69
B	6.5	–	1.05×10^{-2}	440	337	0
(b)						
A	6.5	25.9	4×10^{-3}	1150	8.0	0.35
B	6.5	–	6.1×10^{-1}	8	226.4	0

Results of hydrogen peroxide decomposition tests given as: calculated kinetic constant of hydrogen peroxide decomposition, hydrogen peroxide lifetime for (a) soil 1 and (b) soil 2. Results of TCE oxidation tests given as: TCE residual concentration after 24 h reaction time and TCE degradation yield corresponding to a 99% degradation for (a) soil 1 and (b) soil 2.

ual TCE concentration at the end of the treatment, and TCE degradation yield defined as the ratio among the difference between initial TCE concentration and TCE concentration corresponding to a 99% degradation and the time required to achieve a 99% TCE degradation. This ratio is clearly equal to zero for all operating conditions where 99% TCE reduction was not achieved.

As far as soil 1 is concerned, by comparing the H_2O_2 lifetimes and the TCE oxidation data, it is clear that the latter were in agreement with those expected by the reactivity scale based upon H_2O_2 lifetime. Namely, case A with the longer H_2O_2 lifetime was also the only one allowing for a more than 99% TCE degradation, whereas the TCE residual concentration was higher in case B, characterized by smaller H_2O_2 lifetimes. The same behavior was observed for soil 2, even if with different absolute values, again confirming the different behavior of the two soils already exhibited by the H_2O_2 decomposition results.

The larger TCE removal observed in case A, i.e. when a phosphate salt as stabilizer was added, may be attributed to the higher stability of H_2O_2 with respect to that observed in case B, when no stabilizer was used. Such a stability is due to the capacity of phosphate salts to inhibit the hydrogen peroxide decomposition reactions, that are catalyzed by mineral surfaces, possibly by affecting their surface charge or redox potential at the mineral surface [15]. Since the TCE degradation is a function of the availability of hydroxyl radicals in the reaction system, a longer H_2O_2 residence time means lower concentrations of the radical, but available for a longer period of time. This results in an overall larger extent of TCE degradation in the stabilized system. On the contrary, in the absence of phosphate, hydrogen peroxide is depleted in a short period of time. This results in the production of hydroxyl radicals only for a rather short times, that is not suitable to achieve an effective TCE degradation. It is also worth mentioning that in some conditions, stabilized hydrogen peroxide was also observed to show a higher rate of hydroxyl radicals production than the un-stabilized system, in spite of the lower hydrogen peroxide decomposition rates in the stabilized system [15]. This takes place although phosphate salts may act as a radical scavenger by quenching hydroxyl radicals and terminating chain decomposition reactions [15].

3.2. Column tests

The results of hydrogen peroxide decomposition tests in soil columns are reported in Fig. 1. In this case the tests were limited to soil 1, since it is characterized by a higher permeability and is more suitable for performing column tests. The H_2O_2 concentration values obtained at the outlet of 10, 20, and 30 cm columns are reported in the form of concentration profiles versus column depth. The profile reported in Fig. 1a was obtained after 10 min of H_2O_2 continuous flow through the column, whereas those reported in Fig. 1b correspond to a 180 min flowing time. Hydrogen peroxide concentration was observed to decrease along the column, with a 75% decomposition at 30 cm depth after 10 min, that increased to almost 95% after 180 min. The decomposition was much slower when a stabilizer was added. Namely, only 25% of the incoming hydrogen peroxide was decomposed at 30 cm depth after 10 min, whereas a slight 10% decomposition was observed after 180 min operation. These results clearly confirm the indications of the slurry experiments, showing a positive effect of the stabilizer in increasing the hydrogen peroxide stability. Therefore, also in this case it is possible to predict that the operating condition with the stabilizer should be more effective for the oxidation process. Besides, the obtained results also show that the stabilizing effect increases with time, i.e. with the number of H_2O_2 pore volumes fed to the column, with very promising indications for in situ application. On the contrary, the stability of H_2O_2 alone was observed to decrease with time, thus indicating that the processes responsible for its decomposition do not loose their effectiveness as more H_2O_2 is fed to the column.

The results of TCE oxidation experiments are reported in Fig. 2 and Table 3. In Fig. 2a and b, the TCE concentration measured at increasing times at the outlet of 20 and 30 cm column, respectively, are reported in the form of elution profiles. It can be noticed that the largest amount of TCE was eluted, when water only was used as desorbent. As reported in Table 3, the amount eluted was equal to 78 and 68% of the amount initially adsorbed on the soil, in the 20 and 30 cm column, respectively. The TCE recovery in the liquid phase was much lower when an hydrogen peroxide solution was fed to the 20 and 30 cm columns (20 and 18%, respectively), whereas when a stabilized H_2O_2 solution was used interme-

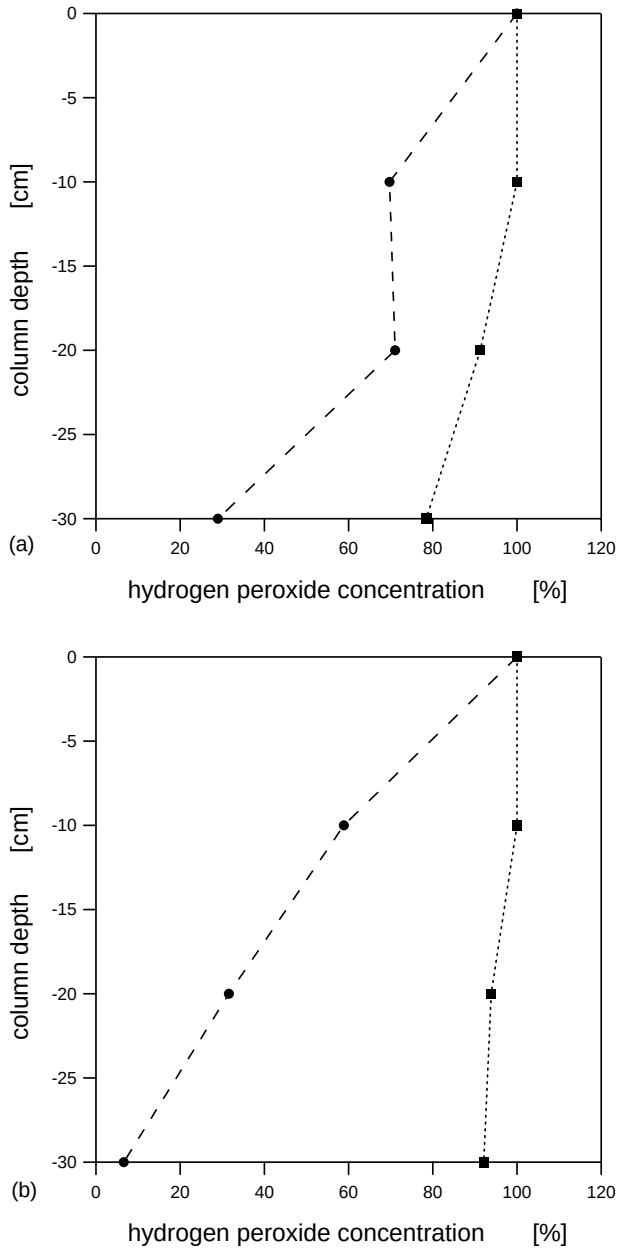

Fig. 1. Hydrogen peroxide concentration profiles in soil 1 columns, after (a) 10 min and (b) 180 min flow. Inlet conditions: $[H_2O_2] = 2\%$; flow rate: 4.5 ml/min; (●), H_2O_2 only; and (■), $H_2O_2 + KH_2PO_4$ (25.9 mM).

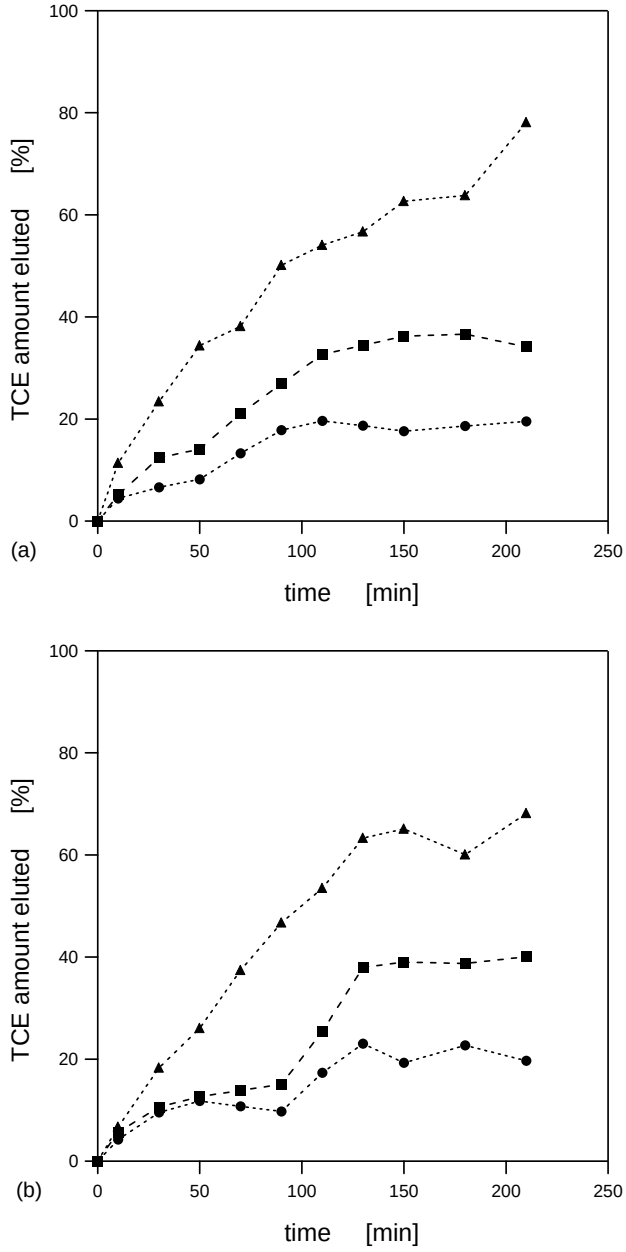

Fig. 2. TCE amount (in percent with respect to the initial quantity in the contaminated soil) eluted from soil 1 column at increasing treatment times: (▲) with H_2O (desorption), (●) with H_2O_2, and (■) with $H_2O_2 + KH_2PO_4$ (25.9 mM). Inlet conditions: $[H_2O_2] = 2\%$, flow rate: 4.5 ml/min; (a) 20 cm column; and (b) 30 cm column.

Table 3
Mass balance of TCE in (a) 20 cm and (b) 30 cm soil 1 columns

Reagent mixture	Desorbed TCE (%)	Residual TCE on soil (%)	Unaccountable TCE (%)	Treated TCE (%)
(a)				
H_2O (desorption)	78	8	14	–
H_2O_2 + stabilizer	35	1.5	14	49.5
H_2O_2	18	68	14	–
(b)				
H_2O (desorption)	68	7.2	24.8	–
H_2O_2 + stabilizer	40	5.2	24.8	30
H_2O_2	20	56	14	–

All TCE amounts are reported as percent valuers of the TCE initially present in the contaminated soil (1000 ± 100 mg/kg).

diate recoveries were achieved (35 and 40%). Finally, the soil was analyzed for the residual TCE at the end of the treatment, resulting in a quite low concentration for all operating cases, except when H_2O_2 only was used, where an amount equal to 68 and 56% of the initial TCE amount was found in the 20 and 30 cm column, respectively. As reported in Table 3, these data allowed to close the TCE mass balance, showing that an effective TCE oxidation took place only when stabilized H_2O_2 was fed to the columns. On the contrary, the application of H_2O_2 only proved not to be effective in TCE oxidation, in this case, the lower eluted TCE amount with respect to the desorption case may be possibly explained with the production of large oxygen gas volumes in the column, that probably occupied a large part of the pore volumes, thus reducing the interface between the liquid H_2O_2 solution and the soil.

4. Conclusions

In this work it was confirmed that hydrogen peroxide lifetime is effectively rather well correlated to the contaminant oxidation efficiency, making possible to build a reactivity scale where the higher oxidation efficiencies was assigned to the operating cases characterized by longer hydrogen peroxide lifetimes. With respect to previous results, the validity of the scale was extended to another contaminant (TCE), but also from batch scale operation to soil column operation, more closely resembling the true operating conditions of an in situ treatment. The predictions of the reactivity scale were then confirmed by the results of TCE oxidation experiments, that generally resulted faster and more efficient whenever the predicted oxidation efficiency was higher.

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