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Hydrogen peroxide lifetime as an indicator of the efficiency of 3-chlorophenol Fenton's and Fenton-like oxidation in soils

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Abstract

In this work the possibility of using the hydrogen peroxide lifetime as indicator of the oxidation efficiency of Fenton's and Fenton-like processes for soil treatment was explored. A reactivity scale, in terms of the oxidizing power in the different tested operating conditions (pH, iron sulfate concentration and stabilizer concentration) was built for each soil as a function of the hydrogen peroxide lifetime. Its validity was then confirmed through 3-chlorophenol Fenton's and Fenton-like slurry-phase oxidation experiments. The proposed reactivity scale proved to be effective for comparing the different operating conditions for the same soil, but failed when used to compare the oxidation performances for different soils, since the different adsorptive behavior of the tested soils may have influenced the contaminant removal rate.

Keywords: AOPs; 3-Chlorophenol; Hydrogen peroxide; Fenton; Soil

1. Introduction

The soil layer of a large number of sites has been found to be polluted with hazardous compounds, such as chlorinated aliphatics, halogenated phenols and PAHs, which are refractory to biotic degradation processes. Remediation of these contaminated sites cannot be generally achieved through biological processes especially if the initial pollutant's concentration is so high to become toxic for bacteria and other biomasses. In these cases, a

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physico-chemical treatment, eventually coupled with a biological step, shall be considered as a possible alternative process in order to reduce the contaminant concentration below the legislative limits fixed by local authorities [1]. Among these, advanced oxidation processes (AOPs) have become one of the most interesting and promising remediation techniques. A review of AOPs application to in situ chemical treatment of contaminated soils and groundwater was provided by Yin and Allen [2]. Their operational principle is based on the idea of generating a pool of oxidizing species in the subsurface environment. The different AOPs 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 [3]; also ozone has been shown to readily oxidize organic compounds [4]. The oxidation of recalcitrant substances can be also achieved by electrochemical peroxidation process (ECP) in which iron is electrochemically generated by steel electrodes [5–7]. It has to be observed that all these references are related to organic compounds in aqueous solution.

One of the more typical AOP is based on the property of hydrogen peroxide to generate hydroxyl radicals by reacting with ferrous ions in the well-known Fenton's reaction [8]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$$

The possibility of applying this process to contaminated soils was first demonstrated by Watts et al. [9] in batch lab-scale experiments and later by Ravikumar and Gurol [10] with sand-packed column tests and by Kakarla and Watts [11] with soil-packed column tests. Ho et al. [12] 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. [13], 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 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 [10]. 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 [10,11]. The influence of the operating conditions on the oxidation performances, in terms of contaminant degradation, were assessed by many authors [9,14]; namely, the optimal pH value was found to be between 2 and 3, whereas the optimal ratio between hydrogen peroxide and iron sulfate was observed to depend upon different parameters, such as the types of soil and pollutant. The decomposition of hydrogen peroxide in subsurface environments was also studied, even if in model systems [15]. 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. The introduction of a more readily measurable indicator of the oxidation efficiency could greatly simplify at least the first screening phase of this procedure, allowing to reduce the number of operating cases to be tested completely. Hydroxyl radicals, produced by hydrogen peroxide decomposition through reaction (1), could represent an ideal indicator, since they are directly responsible for the contaminant oxidation in Fenton's and

Fenton-like processes. Nevertheless, their detection is in principle very difficult and uncertain, due to their high reactivity and instability; besides, the methods developed to quantify hydroxyl radicals by means of appropriate scavengers [16] again would require time consuming extraction/analytical procedures. Even if hydrogen peroxide decomposition in soil systems may take place through other paths than reaction (1) [15] and granted that hydroxyl radicals may also be scavenged by other species than the target contaminants (i.e. the soil organic fraction), the concentration of hydroxyl radicals is surely a function of hydrogen peroxide in the system. Therefore, in this work we want to assess that the efficiency of Fenton's and Fenton-like processes may be correlated to and somehow predicted through simple and fast hydrogen peroxide decomposition experiments; in this approach, hydrogen peroxide lifetime is proposed as a possible indicator of the oxidation efficiency of the reaction system.

To this aim, slurry-phase hydrogen peroxide decomposition kinetics were performed with two different soils at different operating conditions, by modifying some key parameters, such as pH, iron sulfate concentration, hydrogen peroxide concentration and stabilizer concentration. In this way a reactivity scale, in terms of the hydrogen peroxide lifetime in the different tested operating conditions, was built for each soil. Then, the validity of such scale was confirmed for each soil by comparison with the removal efficiencies measured in 3-chlorophenol (3-CP) Fenton's and Fenton-like oxidation experiments, performed at the same operating conditions of the hydrogen peroxide decomposition tests.

2. Materials and methods

2.1. Reagents

Hydrogen peroxide (30%), iron(II) sulfate, 3-CP (99% pure), 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); 2-bromophenol (purity higher than 98%) used as internal standard for gas chromatography–flame ionization detection (GC–FID) analysis, 2′-chloro-2,5-dihydroxybiphenyl (95% pure) and 2-2′-dihydroxybiphenyl (99% pure) used as standard for GC–MS analysis, were purchased from Sigma–Aldrich (Steinheim, 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 in San Policarpo, whereas soil 2 was collected from a cave near Nemi, situated in a volcanic area. Preliminary extraction tests indicated that phenols concentration in both soil types was below the detection limit. The total organic carbon (TOC) measured following the Walkey–Black procedure [17], was 0.9% for soil 1, whereas it was 6.5% 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, reported in Table 1, clearly indicated that soil 1 is characterized by a much higher clay content than soil 2, which is mainly composed of sand and loam. Therefore, soil 1 was classified as a clay sand with loam, whereas soil 2 as a loamy sand. The composition of the two soils is reported

Table 1
Composition (in percentage) of soils 1 and 2

Fraction	Soil 1	Soil 2
Grave	4.03	10.63
Sand	45.05	53.97
Loam	26.92	34.50
Clay	24.00	0.90

in Table 1. Iron and manganese concentrations in different chemical forms, determined by selective extraction following the Tessier method [18] and measuring the selective leachate with a 3030 B spectrophotometer (Perkin-Elmer, Norwalk, CT), are reported in Table 2. The scheme in widespread use, known as "Tessier's", differentiates the following five groups of elements: easily exchangeable; bound to carbonates; bound to Fe or Mn oxides; bound to organic matter or as sulphides; and that present in the residual fraction. Generally, the first four fractions represent hydrogenous or biogenous origins [19], rather than lithogenous as indicated by the fifth fraction. The residual solid in the fifth fraction should contain mainly primary and secondary minerals, incorporating elements in their crystalline structure forms which would be hardly available. As shown in Table 2, the more readily available source of soluble iron for the Fenton's reaction, that is the easily exchangeable one, was found to be higher for soil 2, as well as the iron oxides. On the contrary, manganese oxides, that are considered among the most active catalysts of hydrogen peroxide decomposition in soils [20], were found to be two times larger in soil 1 than in soil 2. The soil moisture, determined after soil drying at 105 °C for 16 h, was found equal to 5.6 and 7.2% for soils 1 and 2, respectively. Preliminary tests indicated that both soils did not contain 3-CP before contamination was performed.

2.3. Kinetics of hydrogen peroxide degradation and 3-CP oxidation

Kinetics of hydrogen peroxide degradation were studied through batch experiments, performed in 50 ml amber glass vials, kept in continuous agitation (400 rpm) on a multi-position magnetic stirrer, supplied by VELP Scientifica (Italy). The temperature was not controlled,

Table 2
Distribution of the different iron and manganese fractions (in mg/g; according to Tessier differentiation) in soils 1 and 2

	Soil 1		Soil 2	
	Fe	Mn	Fe	Mn
Easily exchangeable	0.0001	0.003	0.006	0.002
Bound to carbonates	0.002	0.003	0.009	0.002
Bound to oxides	8.6	1.05	13.9	0.58
Bound to organic matter or as sulfides	0.076	0.015	0.16	0.009
Residual fraction	19.45	0.276	22.7	0.704
Total	28.1	1.35	36.8	1.30

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 with a given concentration of iron sulfate and hydrochloric acid for pH adjustment. Also monobasic potassium phosphate could be eventually added to the soil slurry. The initial pH of the soil slurry was measured with a portable pHmeter 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 [9]. Then, a sample of the slurry was collected and immediately centrifuged at 4000 rpm 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.

The soils were contaminated with 3-CP by spiking a 250 g sample of soil 1 or 2 with 50 ml of a 5 g/l 3-CP solution, in order to obtain a 3-CP concentration of 1000 mg/kg of dry soil with a final water content of about 20%. Contamination was performed by sparging the 3-CP solution on the soil sample and then by mixing each soil sample to achieve a homogeneous pollutant distribution. The 3-CP oxidation experiments, whose details are reported elsewhere [21], were performed in the same operating conditions used for the hydrogen peroxide experiments. In this case, after centrifugation, both soil and supernatant were analyzed for 3-CP, as described below.

2.4. Batch adsorption tests

Adsorption equilibrium experiments were performed in 50 ml amber glass vials, kept in continuous agitation (400 rpm) on a multi-position magnetic stirrer, supplied by VELP Scientifica (Italy). A 2.5 g soil sample of uncontaminated soil 1 or 2 was added to the vial, together with 12 ml of a 3-CP solution (initial concentration = 50–2000 mg/l) and stirred for 24 h in order to achieve equilibrium. After 24 h equilibration time, a sample of the soil slurry was collected and centrifuged, as described above. The supernatant was then analyzed for 3-CP, providing the 3-CP equilibrium concentration in the liquid phase. The 3-CP concentration in adsorbed phase was determined from a mass balance on 3-CP in the liquid phase.

2.5. Analytical methods

Determination of 3-CP in soil and supernatant was obtained by the SPME technique coupled to GC–FID. The SPME extractions were done using a manual 85 μm polyacrylate SPME device purchased from Supelco (Bellefonte, PA, USA), following the procedure reported by Baciocchi et al. [22] for soil extraction and analysis. The liquid sample was also extracted and analyzed with the same procedure: in this case, a 2 ml sample of supernatant was added to the 35 ml extraction glass used for the SPME extraction. 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. BP5 capillary column (SGE, Ringwood, Australia). The presence of reaction byproducts was determined

through GC–MS analysis performed with a gas chromatograph model HRGC 5160 (Carlo Erba, Italy) coupled to a mass spectrometer model Quattro (VG Micromass, UK), using the same column and analytical conditions described above. All analysis were performed in scan mode.

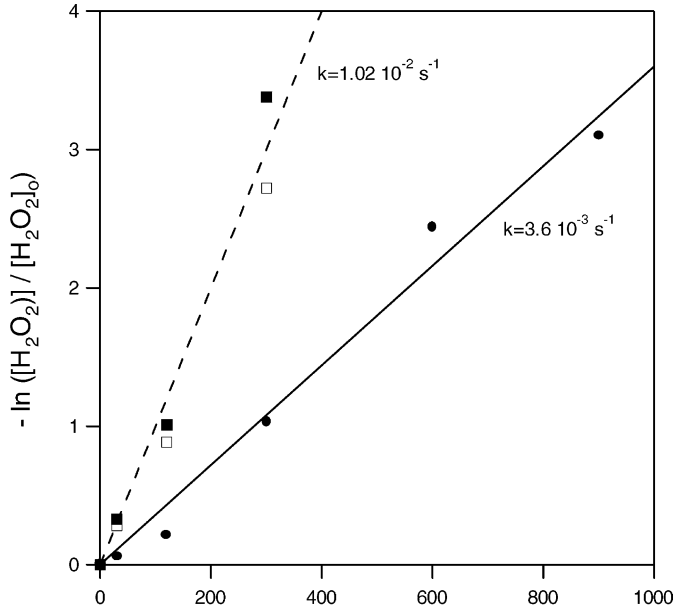
Determination of hydrogen peroxide was performed by the iodometric method [23].

3. Results and discussion

3.1. Kinetics of hydrogen peroxide decomposition

The hydrogen peroxide decomposition data were fitted with a first-order model, in agreement with the literature [14,20]. The correlation coefficient for all datasets ranged between 0.95 and 0.97, with an average of seven experimental points per dataset. The results and the data fitting of hydrogen peroxide decomposition experiments for soil 1, without pH adjustment or addition of iron sulfate, are reported in Fig. 1a for two different initial hydrogen peroxide concentrations, equal to 2.1 and 4.2 vol.%. In these operating conditions, hydrogen peroxide was decomposed at a very fast rate, since no residual hydrogen peroxide could be detected after only 8 min. The hydrogen peroxide decomposition was observed to follow a first-order kinetics, with a kinetic constant around $10^{-2}\,s^{-1}$. The same experiments were then repeated with 2.1 vol.% initial hydrogen peroxide concentration, but now adding iron sulfate as indicated in Fig. 1a. The results, reported again in this figure, clearly indicate that iron sulfate addition slightly decreased the hydrogen peroxide decomposition, with a kinetic constant around $10^{-3}\,s^{-1}$. As shown in Fig. 1b, the pH adjustment was far more efficient in reducing such decomposition rate; operating with pH 2.4, residual hydrogen peroxide was still detected after 24 h and the kinetic constant dropped to around $10^{-5}\,s^{-1}$. Addition of iron sulfate to the slurry did not notably affect hydrogen peroxide decomposition (see Fig. 1b). Finally, the influence of adding a stabilizer (monobasic potassium phosphate) was studied; the results, shown again in Fig. 1b, indicate that the influence of the stabilizer is somewhat comparable with that obtained by adjusting the pH to 2.4. As clearly shown in Fig. 1c and d, the influence of the operating conditions on the hydrogen peroxide lifetime was less effective for soil 2. The kinetic constant of the hydrogen peroxide decomposition reaction was in most experiments around $10^{-5}\,s^{-1}$, except for the test performed without pH adjustment or iron addition, with a $10^{-4}\,s^{-1}$ value (see Fig. 1c). The different behavior observed for hydrogen peroxide decomposition in the tested soils may be correlated to their different composition and texture. If compared to soil 2, soil 1 exhibits a larger specific surface, due to the higher clay presence, and a higher content of manganese oxides, that may both effectively catalyze the hydrogen peroxide decomposition [20].

Fig. 1. Fitting of hydrogen peroxide decomposition data in soil 1 (a and b) and soil 2 (c and d) slurries with first-order kinetics: 2.5 g soil in 12 ml distilled water. (■) $[H_2O_2]$ = 4.2 vol.%, no Fe^{2+}, pH not adjusted, no KH_2PO_4; (□) $[H_2O_2]$ = 2.1 vol.%, no Fe^{2+}, pH not adjusted, no KH_2PO_4; (●) $[H_2O_2]$ = 2.1 vol.%, $[Fe^{2+}]$ = 46 mM, pH not adjusted, no KH_2PO_4; (▼) $[H_2O_2]$ = 2.1 vol.%, no Fe^{2+}, pH not adjusted, $[KH_2PO_4]$ = 26 mM; (◆) $[H_2O_2]$ = 2.1 vol.%, no Fe^{2+}, pH 2.4, no KH_2PO_4; (▲) $[H_2O_2]$ = 2.1 vol.%, $[Fe^{2+}]$ = 46 mM, pH 2.4, no KH_2PO_4.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k=3.6 10-3 s-1
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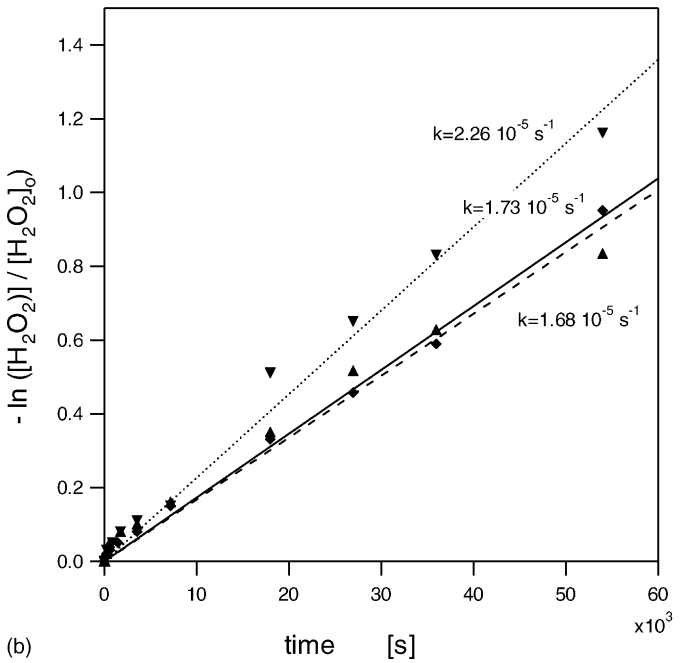
time [s]

(a)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k=1.73 10-5 s-1
k=1.68 10-5 s-1
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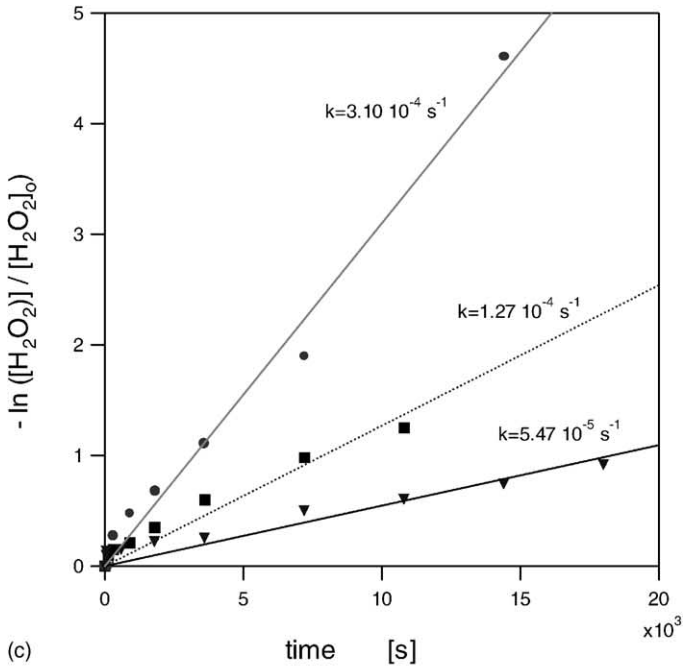
time [s]
x10^3

(b)



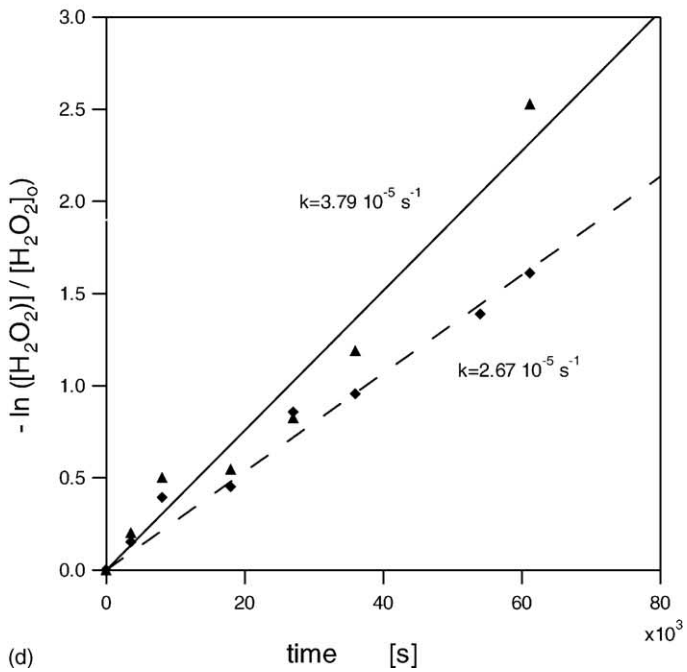


Fig. 1. (*Continued*).

Table 3
Operating conditions of hydrogen peroxide batch tests, calculated kinetic constant of hydrogen peroxide decomposition, hydrogen peroxide lifetime, and hydrogen peroxide and 3-CP time yields for (a) soil 1 and (b) soil 2

Operating case	pH	Fe^{2+} (mM)	Stabilizer (mM)	Kinetic constant (s^{-1})	H_2O_2 lifetime (min)	H_2O_2 decomposition yield (mol/(m^3 h))	3-CP degradation yield (mol/(m^3 h))
(a)							
A	6.5	–	–	1.02×10^{-2}	8	5300	0
B	6.5	3.5	–	3.60×10^{-3}	21	2020	3
C	6.5	–	25.9	2.96×10^{-5}	3400	12.5	0.06
D	2.4	–	–	1.73×10^{-5}	4400	9.6	12
E	2.4	3.5	–	1.68×10^{-5}	4650	9.3	45
(b)							
A	6.5	–	–	1.27×10^{-4}	600	70	0
B	6.5	3.5	–	3.00×10^{-4}	255	326	0
C	6.5	–	25.9	5.47×10^{-5}	1400	30	0.06
D	2.4	–	–	2.67×10^{-5}	2875	15	0.375
E	2.4	3.5	–	3.79×10^{-5}	2025	21	0.13

The values of the first-order kinetic constants of the hydrogen peroxide decomposition experiments are summarized in Table 3. A qualitative reactivity scale is also proposed in the same table, where stronger oxidation efficiency may be attributed to the cases exhibiting higher hydrogen peroxide lifetime. Larger values of hydrogen peroxide lifetime clearly correspond to a higher predicted oxidation efficiency. This scale can be used to obtain a relative prediction of the oxidation performances that can be achieved in different operating conditions; namely, with reference to Table 3, it is possible to expect that conditions C–E, characterized by higher hydrogen peroxide lifetime, should guarantee a more effective oxidation of a pollutant with respect to conditions A and B, where a much lower hydrogen peroxide lifetime was measured. The validity of this scale is in our opinion limited to the comparison of the operating conditions for the same soil. Nevertheless, the possibility of using this scale to compare the reactivity of two different soils in the same operating conditions was also checked, as described in the following section.

For sake of completeness, values for the hydrogen peroxide space time yield treated to a 99% reduction in its concentration are also reported in Table 3. It is clear that larger values for this parameter correspond to lower values of hydrogen peroxide lifetime and thus to a higher predicted oxidation efficiency.

3.2. 3-CP adsorption isotherms

The adsorption equilibrium data of 3-CP on soil 2, reported in Fig. 2, were fitted with a Langmuir-type isotherm:

$$q = \frac{QbC}{1 + bC}$$

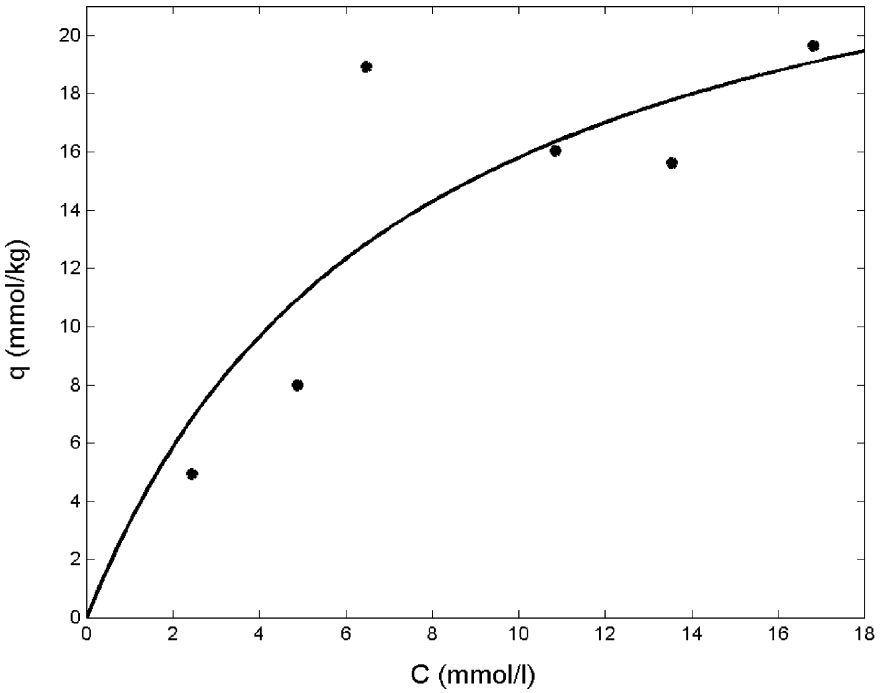


Fig. 2. Adsorption isotherm (continuous line) and equilibrium experimental data (●) of 3-CP on soil 2.

where q is the adsorbed phase concentration (mmol/kg), C the liquid phase concentration (mmol/l), Q the adsorbed phase saturation concentration and b the Henry's constant (l/mmol), affecting the adsorption at low concentration. The calculated saturation concentration was equal to 27.4 mmol/kg, equivalent to 3.5 g/kg, for a liquid phase concentration of about 2.5 g/l. On the contrary, in the same liquid phase concentration range, the adsorbed amount of 3-CP on soil 1 was too low to be measured with sufficient precision. This result, indicating that the adsorption capacity of soil 2 is much greater than that of soil 1, can be probably explained with the much higher organic carbon content of soil 2 with respect to soil 1.

3.3. *Influence of iron amendment*

The efficacy of iron amendment in driving the reaction towards a Fenton-controlled condition was investigated by performing different 3-CP oxidation batch tests at the same operating conditions, except for iron(II) concentration. The data reported in Fig. 3a for soil 1, were obtained at a 1 vol.% initial hydrogen peroxide concentration, whereas data reported in Fig. 3b for soil 2 were obtained at a 2.1 vol.% initial hydrogen peroxide concentration. The results clearly show the positive effect of iron addition for both soils. Namely, as far as soil 1 is concerned, complete oxidation was achieved only for a 3.5 mM iron(II) concentration. Complete oxidation was not achieved for soil 2, since in this case the highest organic fraction

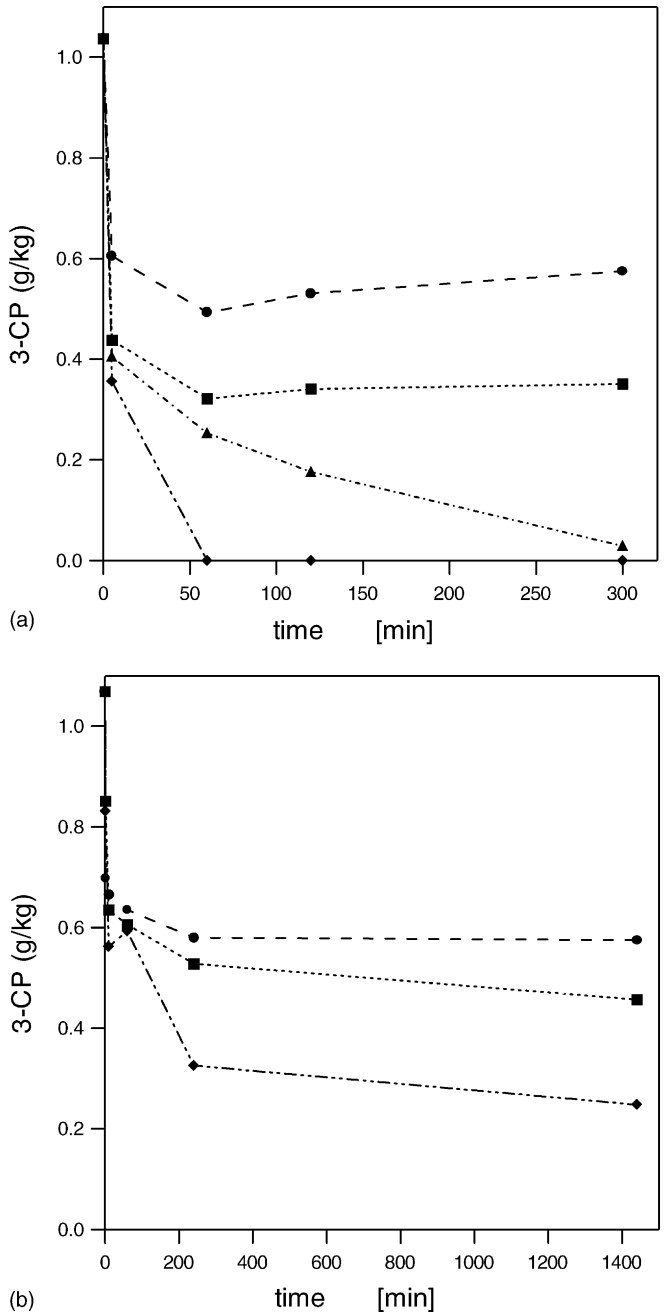


Fig. 3. Kinetics of 3-CP degradation: (a) 2.5 g soil 1 in 12 ml distilled water, pH not adjusted, $[H_2O_2] = 1$ vol.%; (b) 2.5 g soil 2 in 12 ml distilled water, pH not adjusted, $[H_2O_2] = 2.1$ vol.%. (●) No Fe^{2+}; (■) $[Fe^{2+}] = 0.9$ mM; (▲) $[Fe^{2+}] = 1.8$ mM; (◆) $[Fe^{2+}] = 3.5$ mM.

and the already discussed different adsorption behavior may have negatively affected the oxidation performance.

3.4. 3-CP oxidation versus hydrogen peroxide decomposition

The validity of the proposed reactivity scale was assessed by comparing its predictions with the results of 3-CP oxidation experiments, performed on both soils 1 and 2. The efficiency of 3-CP oxidation was given in terms of 3-CP degradation space time yield treated to a 99% reduction in its concentration. The 3-CP oxidation and hydrogen peroxide degradation kinetics in a soil 1 slurry with 2.1 vol.% hydrogen peroxide, without pH adjustment or iron sulfate addition, corresponding to case A in Table 3a, are compared in Fig. 4a. It is worth noting that 3-CP oxidation proceeds at a very fast rate as long as hydrogen peroxide is available in the system, but it readily stops when hydrogen peroxide is completely decomposed (lifetime: 8 min). On the contrary, the kinetics obtained in the same conditions but at pH 2.4, corresponding to case E in Table 3a and shown in Fig. 5a, indicate that 3-CP is completely and readily oxidized, while hydrogen peroxide decomposition proceeds with extremely low rate (lifetime: 4650 min). As shown in Table 3, this result is confirmed by the values of 3-CP degradation yield, that is higher in case E than in case A. This result is in agreement with the proposed reactivity scale, since by comparing cases A and E in Table 3, it is confirmed that an higher 3-CP degradation yield corresponds to a higher hydrogen peroxide lifetime.

Similar results were obtained for soil 2, as shown by comparing Figs. 4b and 5b. Almost 100% 3-CP oxidation was observed (see Fig. 5b) at acidic pH conditions (case E in Table 3b), when the hydrogen peroxide lifetime was 2875 min, whereas it was only around 60% without pH adjustment (see Fig. 5a and case A in Table 3b) when the hydrogen peroxide lifetime was equal to 600 min. The correlation between predicted and experimental 3-CP oxidation efficiency was confirmed by comparing the results of experiments on soil 1 obtained at different iron concentrations. Namely, the results reported in Fig. 6a clearly indicate that in the iron-amended slurry (case B in Table 3a) the 3-CP degradation yield was higher than in the slurry without iron (case A in Table 3a). This result is again in agreement with the hydrogen peroxide lifetime, which is equal to 21 min in the iron-amended sample (case B), whereas it is lower and equal to 8 min in the not amended one (case A). The results of the same experiments performed on soil 2, shown in Fig. 6b, indicate that the influence of iron addition on 3-CP oxidation efficiency is in this case rather poor, since in both cases the 3-CP space time yield was zero. This evidence is in agreement with the predicted hydrogen peroxide lifetime in the iron-amended (case B in Table 3b) and not amended (case A in Table 3b) samples, that were both relatively low. Finally, also the influence of the stabilizer on the oxidation performances could be correlated to its effect on hydrogen peroxide lifetime. This conclusion can be drawn by comparing the kinetics of hydrogen peroxide decomposition and 3-CP oxidation with stabilizer addition, reported in Fig. 7, with those obtained without stabilizer addition, reported in Fig. 4. When the stabilizer is added to the slurry, complete 3-CP oxidation is obtained, as shown in Fig. 7a and b for soils 1 and 2, respectively. This evidence is again in agreement with the hydrogen peroxide lifetimes, that were equal to 3400 and 1400 min for soils 1 and 2, respectively, in the stabilizer-amended samples (case C in Table 3a and b), whereas they were equal to

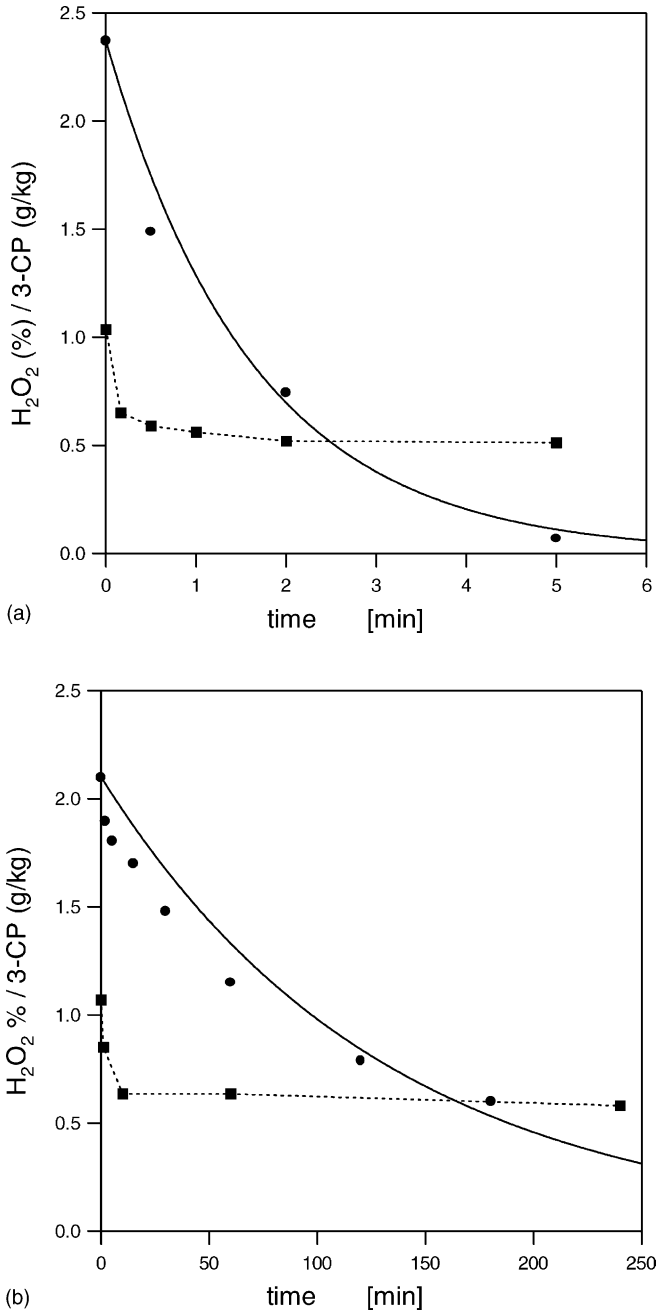


Fig. 4. Comparison between the kinetics of 3-CP (■) oxidation and hydrogen peroxide (●) decomposition in (a) soil 1 and (b) soil 2 slurries: 2.5 g soil in 12 ml distilled water, pH not adjusted, $[H_2O_2] = 2.1$ vol.%, no Fe^{2+} added, no KH_2PO_4.

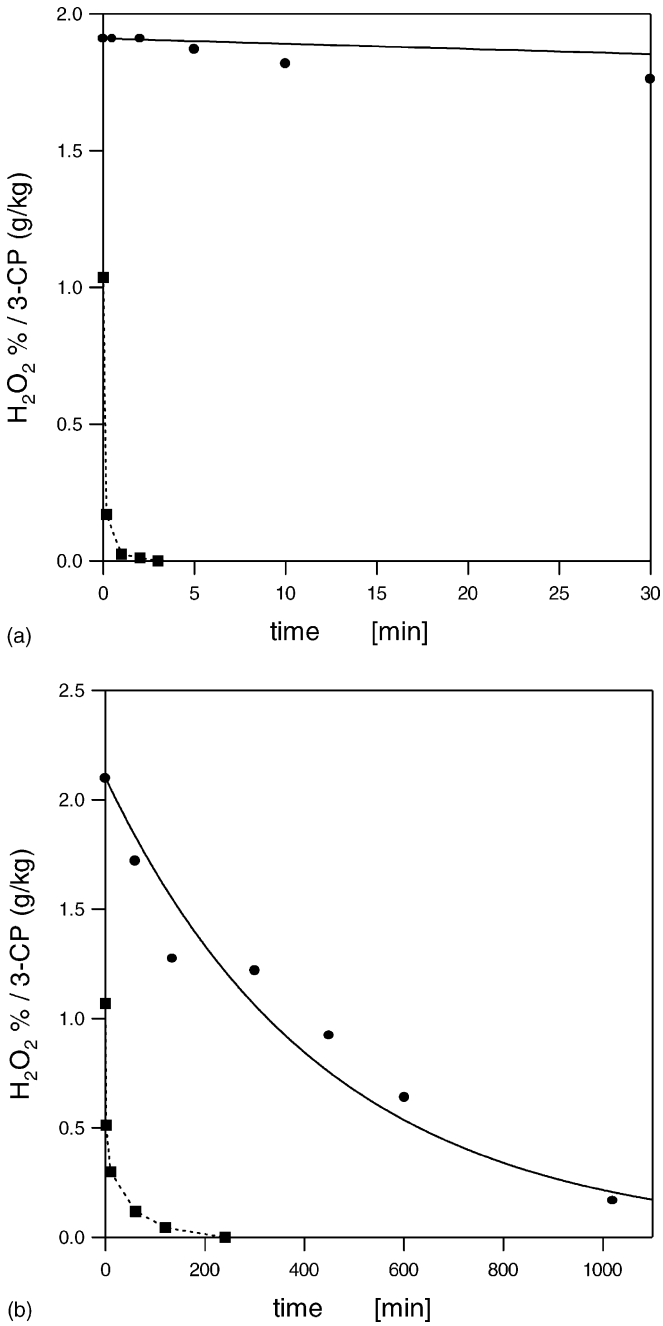


Fig. 5. Comparison between the kinetics of 3-CP (■) oxidation and hydrogen peroxide (●) decomposition in (a) soil 1 and (b) soil 2 slurries: 2.5 g soil in 12 ml distilled water, pH 2.4, $[H_2O_2] = 2.1$ vol.%, $[Fe^{2+}] = 3.5$ mM, no KH_2PO_4.

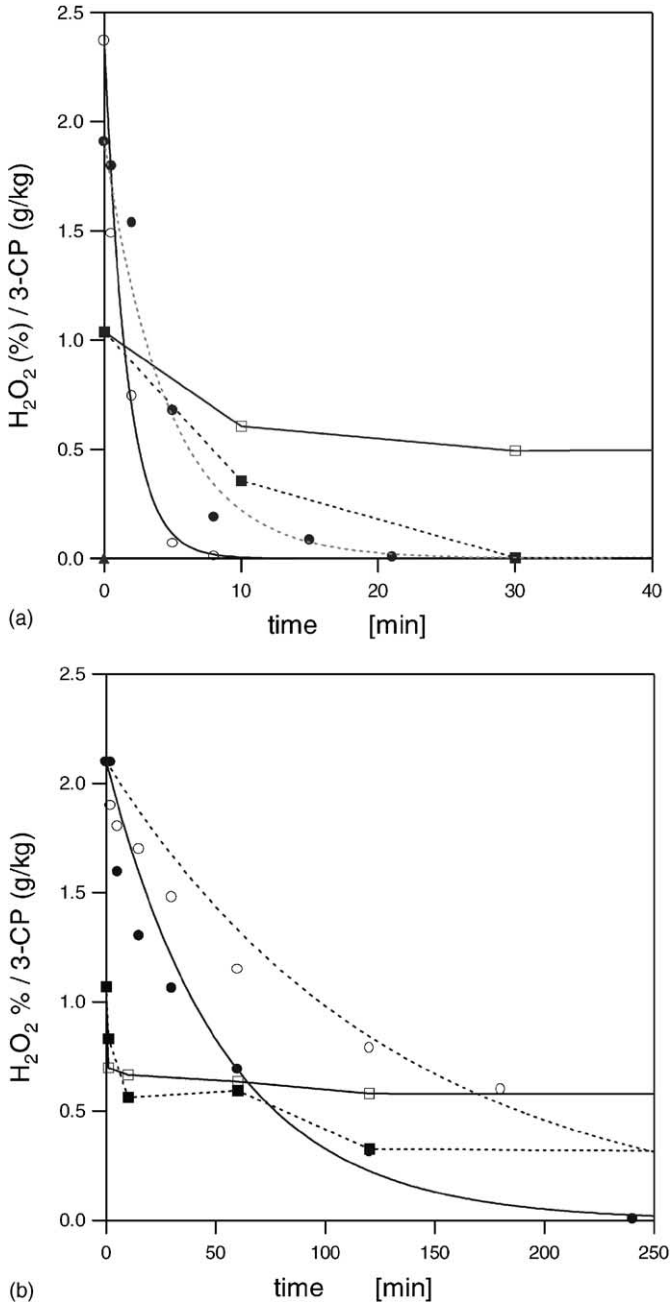


Fig. 6. Influence of iron addition on the kinetics of 3-CP (□, ■) oxidation and hydrogen peroxide (○, ●) decomposition in (a) soil 1 and (b) soil 2 slurries: 2.5 g soil in 12 ml distilled water, pH not adjusted, no KH_2PO_4, $[H_2O_2] = 2.1$ vol.%. (■, ●) $[Fe^{2+}] = 3.5$ mM; (□, ○) no Fe^{2+} added.

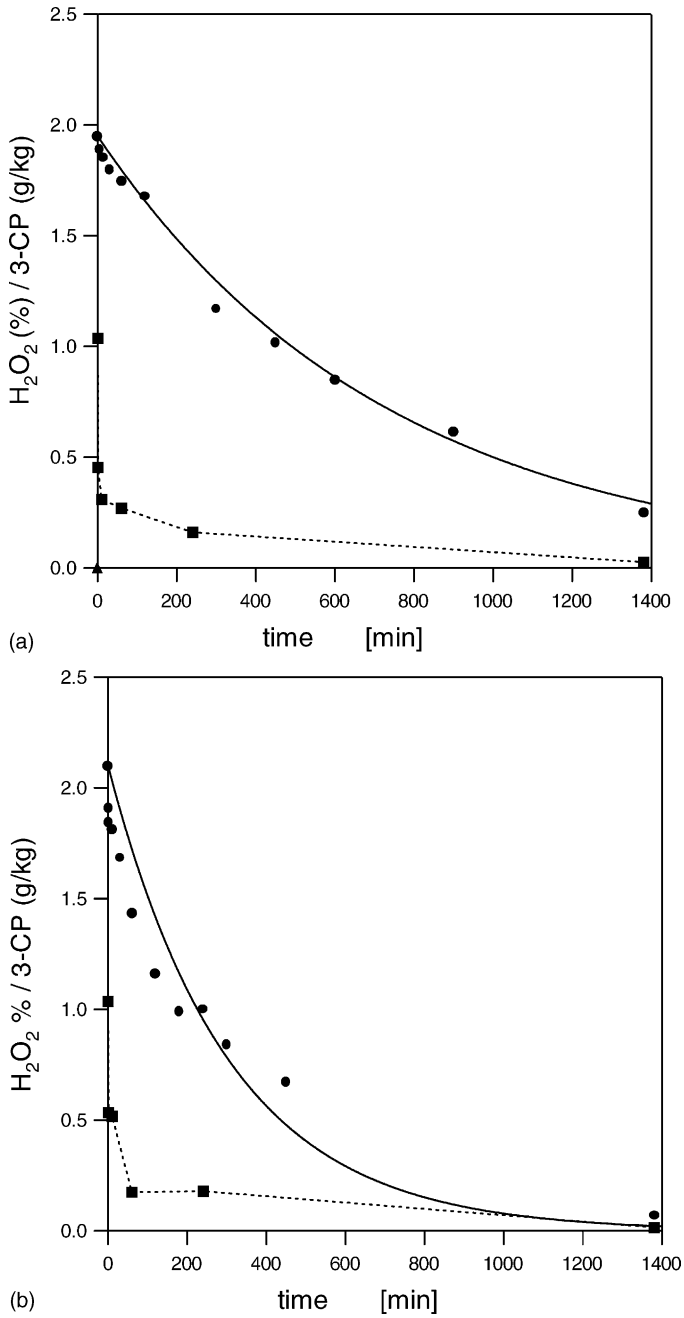


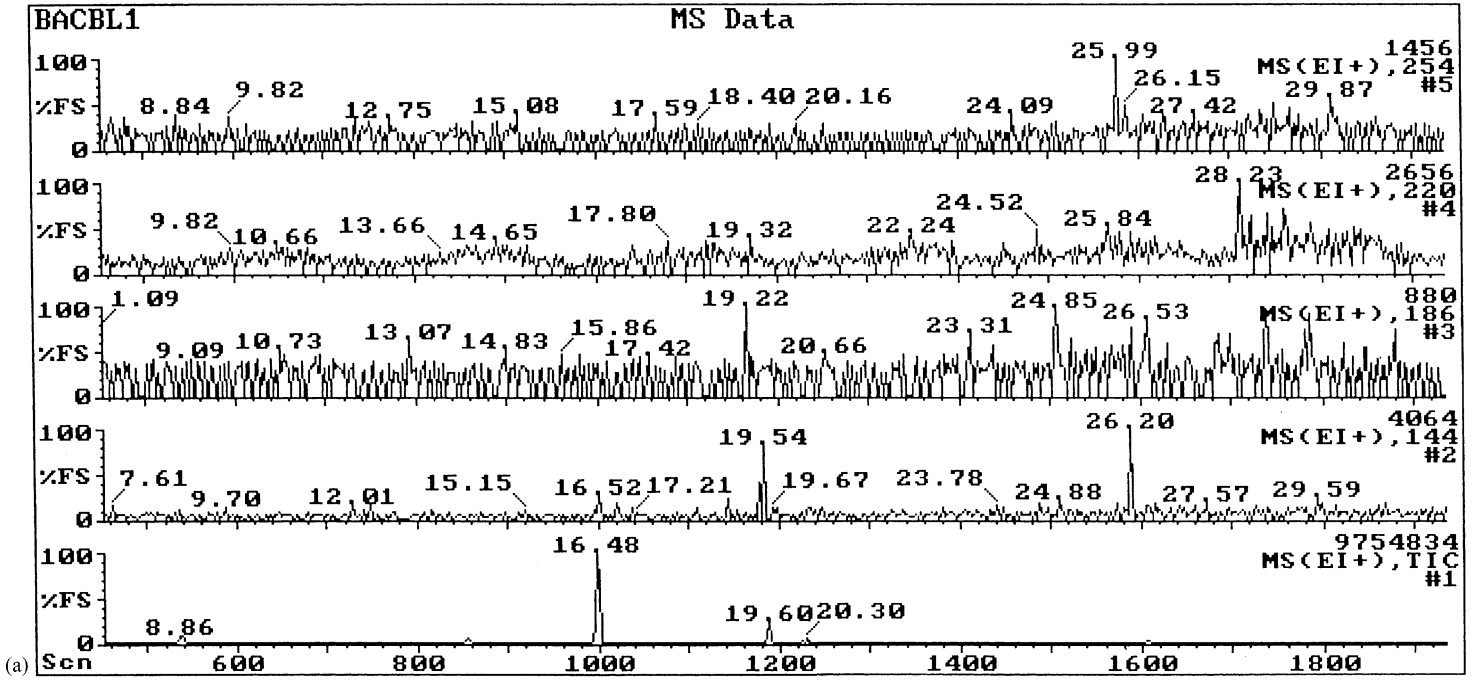
Fig. 7. Comparison between the kinetics of 3-CP (■) oxidation and hydrogen peroxide (●) decomposition in (a) soil 1 and (b) soil 2 slurries: 2.5 g soil in 12 ml distilled water, pH not adjusted, $[H_2O_2] = 2.1$ vol.%, no Fe^{2+} added, $[KH_2PO_4] = 25.9$ mM.

8 and 600 min, respectively, when no stabilizer was added (case A in Table 3a and b). By looking at Table 3, the correlation between longer hydrogen peroxide lifetimes and larger 3-CP degradation yields has only one exception, represented by cases B and C for soil 1. Nevertheless, it is important to point out that, even if different yields were measured, both conditions met complete 3-CP oxidation. It is also worth pointing out that, despite a very near H_2O_2 decomposition yield, the 3-CP degradation yield observed in cases D and E were much larger than in case C, especially as far as soil 1 is concerned. This may be explained with the different H_2O_2 decomposition pathways, that may either take place through the Fenton's mechanism, leading to hydroxyl radicals formation, or through "not productive" mechanisms, such as disproportion to water and oxygen. Since the latter process is known to prevail at nearly neutral pH [15], in these conditions hydroxyl radicals production rate is probably low, thus determining the low 3-CP degradation yield, observed in case C. On the contrary, the Fenton's pathway is predominant at acidic pH values, thus increasing the hydroxyl radicals production rate and consequently the 3-CP degradation yield, as observed in cases D and E.

The different behavior of the two soils, discussed in the previous section with reference to the hydrogen peroxide decomposition, was also observed in the 3-CP degradation experiments. In the tested operating conditions, the 3-CP oxidation was generally faster in soil 1 than in soil 2, even if the removal efficiency at the end of the treatment was in most cases approximately the same for the two soils or sometimes larger for soil 1. This behavior is not in agreement with the predictions of the reactivity scale based on the hydrogen peroxide lifetime, if these were used to compare the 3-CP degradation yields obtained on different soils. Namely, hydrogen peroxide lifetime in case E (see Table 3) is equal to 2025 min for soil 2 against 4650 min for soil 1, whereas a two order of magnitude difference between the 3-CP degradation yields in the two cases is observed. This is probably due to the different hydroxyl radicals scavenging by the two soils; namely, in soil 2, which is characterized by a very high TOC, the hydroxyl radicals oxidize the organic matter and are less available for 3-CP oxidation with respect to soil 1, whose TOC content is much lower. This turns out in a much lower 3-CP degradation yield observed for soil 2. Besides, the different adsorptive behavior between soils 1 and 2 also plays an important role: as reported above, 3-CP was more strongly adsorbed on soil 2. Since the oxidation reaction takes place mainly in the aqueous phase, its rate is probably controlled by the desorption step that is more difficult for soil 2 than for soil 1. This explanation is also supported by the experimental evidence that when 3-CP was not completely removed, the residual contaminant was never found in soil 1 samples, but in the supernatant only; on the contrary, when soil 2 was treated, 3-CP was detected in both soil and supernatant. Finally, it is worth pointing out that also the different adsorptive behavior is mainly due to the different TOC content of the two soils.

3.5. Byproducts of 3-CP oxidation

The performance of 3-CP oxidation were also evaluated with regard to the possible formation of byproducts. The GC–MS chromatograms corresponding to two of the tested operating conditions after a 3 h reaction time are reported in Figs. 8 and 9 for soils 1 and 2, respectively, together with the chromatograms corresponding to blank samples. These conditions correspond to cases A and E in Table 3, that represent the two limiting conditions



(a)

Fig. 8. Total ion current (TIC) and single ion current (MW = 144, 186, 220 and 254) GC–MS chromatograms of soil 1 slurry supernatant after 3 h reaction time: (a) blank sample; (b) case A in Table 3; (c) case E in Table 3.

(b)

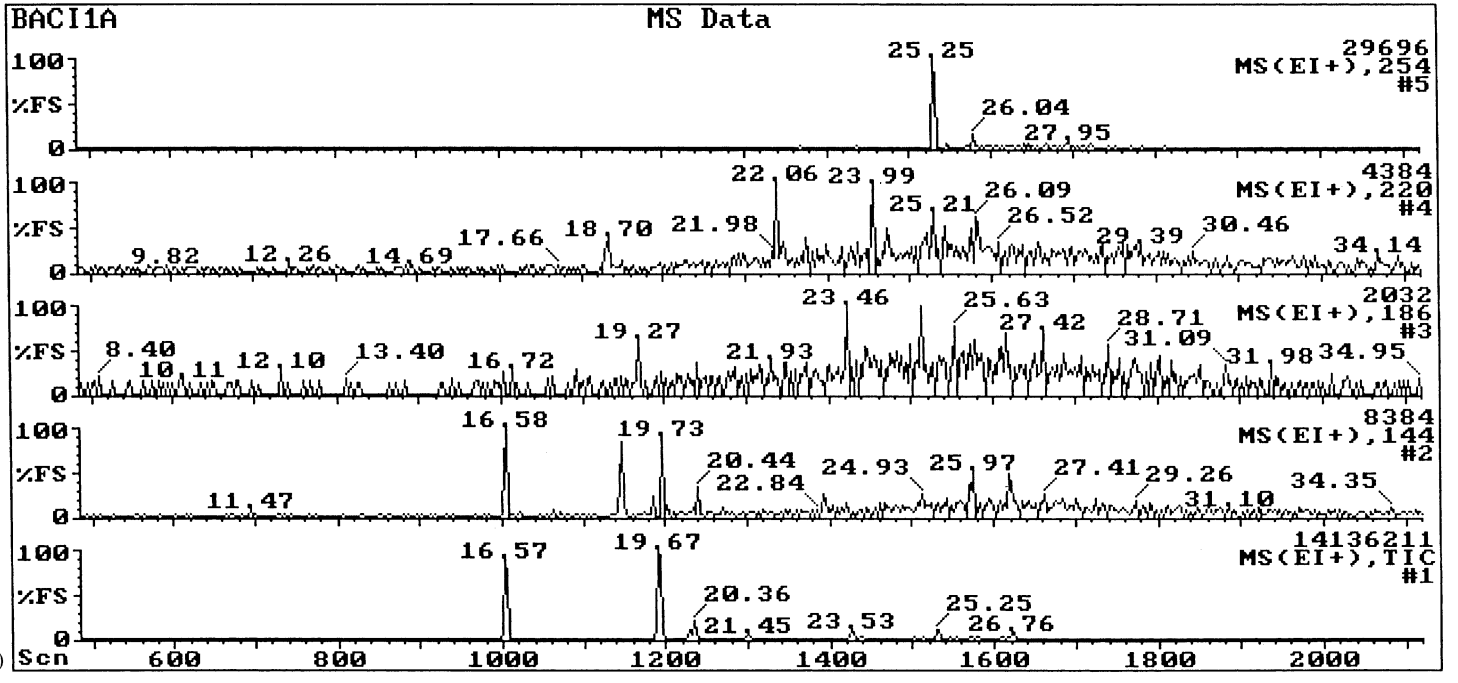


Fig. 8. (*Continued*).

(c)

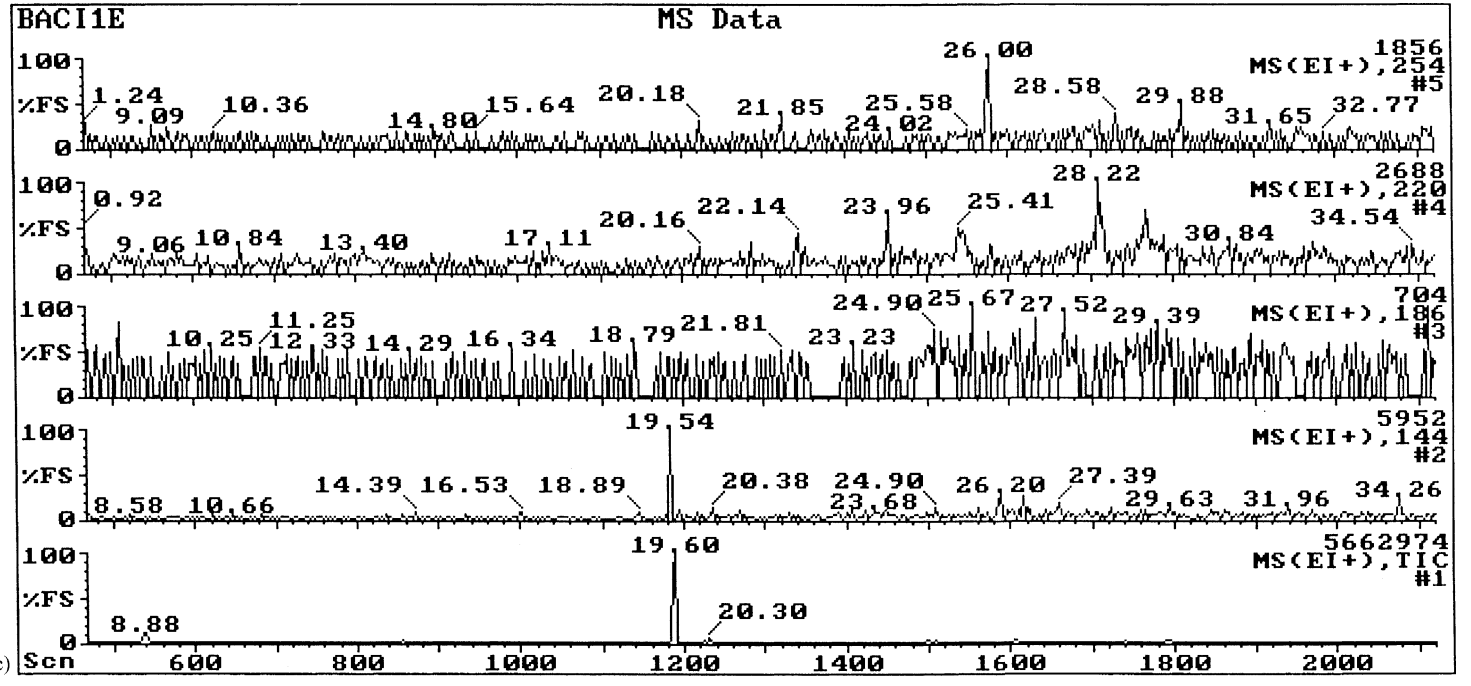
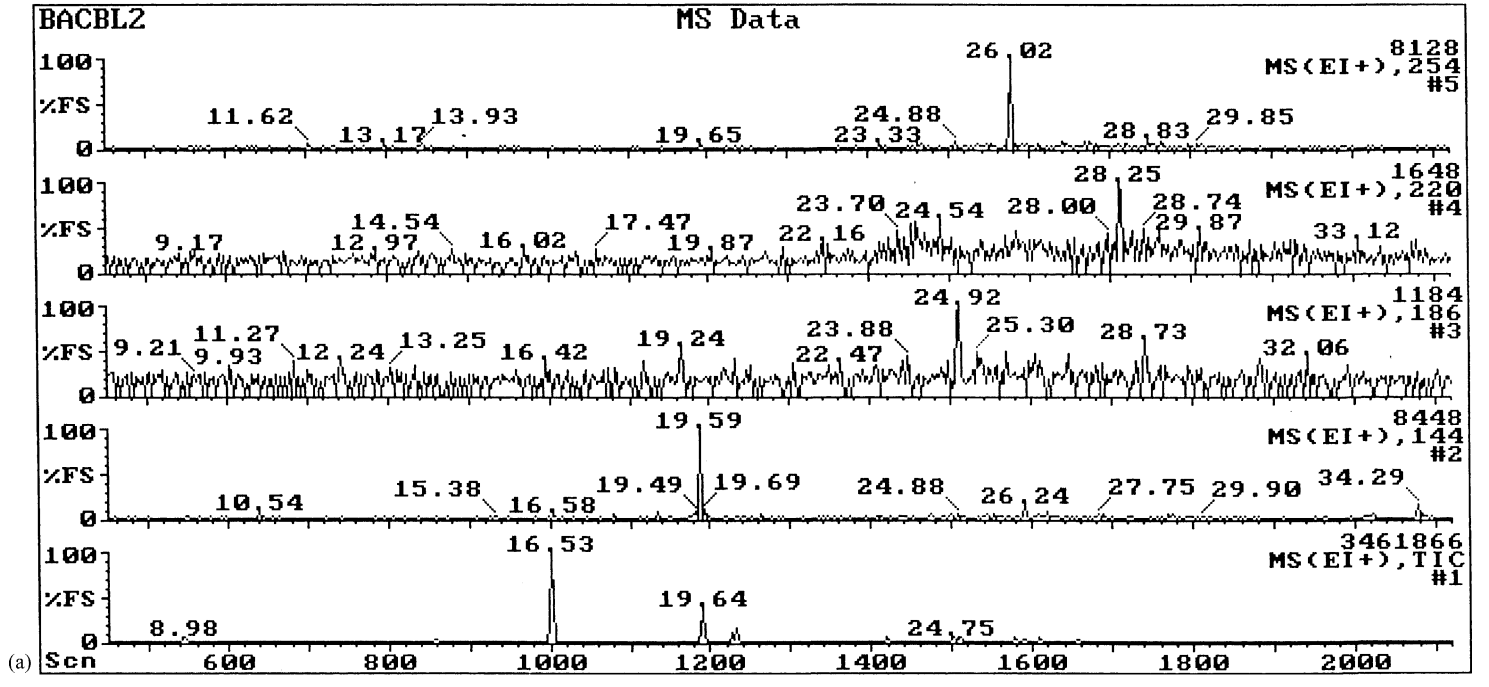


Fig. 8. (*Continued*).



(a)

Fig. 9. Total ion current (TIC) and single ion current (MW = 144, 186, 220 and 254) GC–MS chromatograms of soil 2 slurry supernatant after 3 h reaction time: (a) blank sample; (b) case A in Table 3; (c) case E in Table 3.

(b)

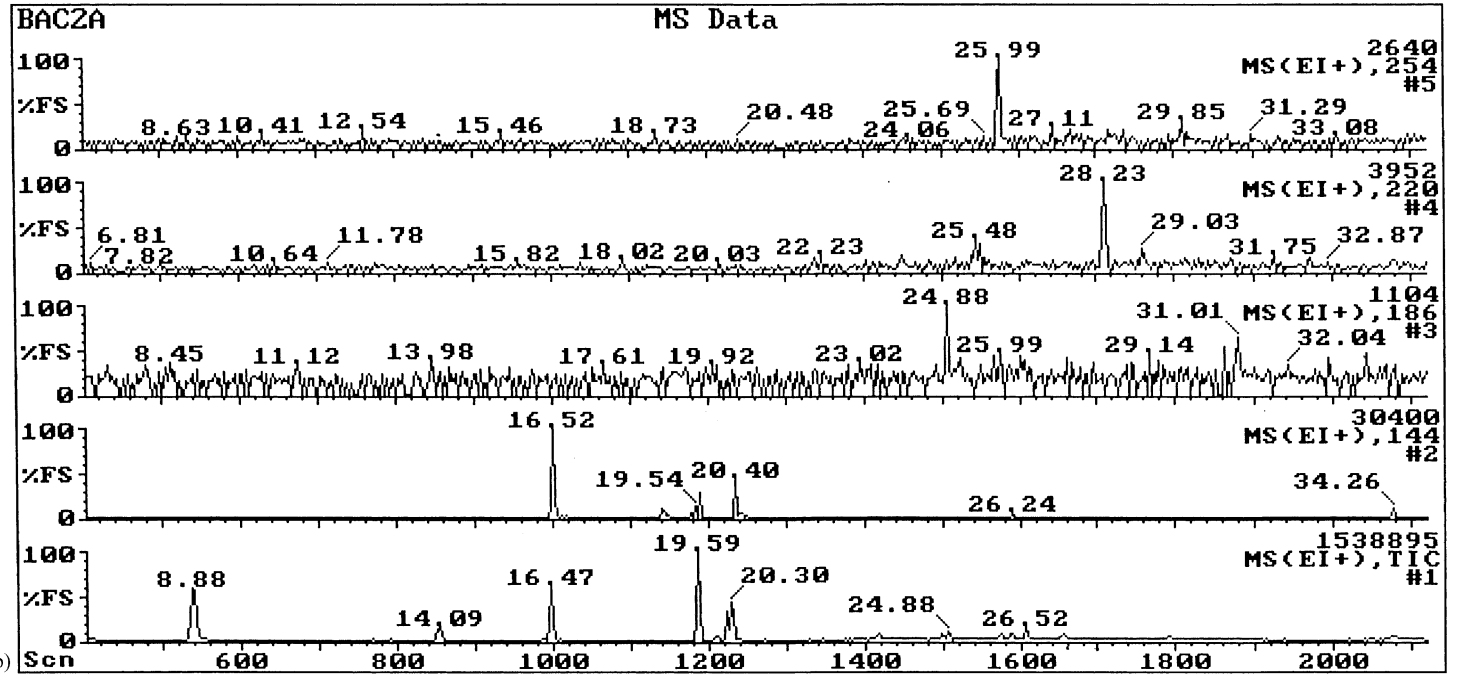


Fig. 9. (*Continued*).

(c)

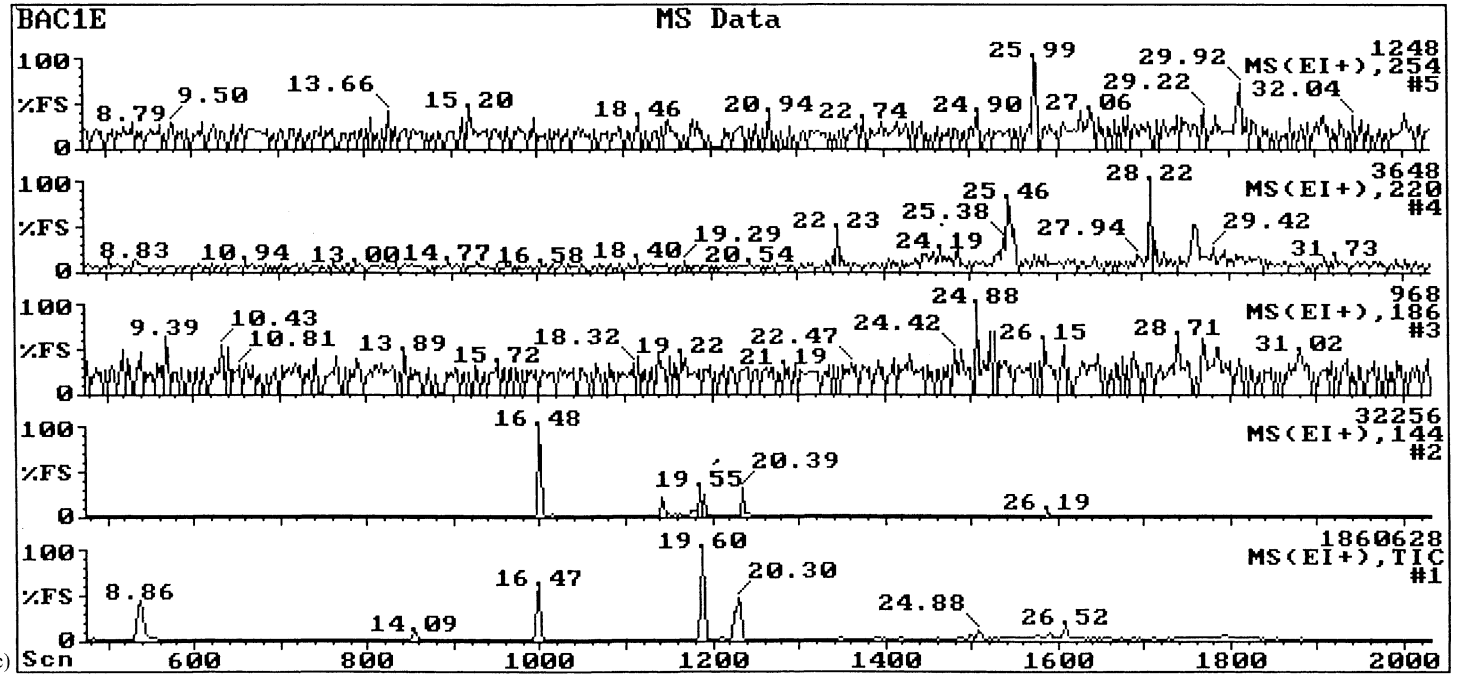


Fig. 9. (*Continued*).

in terms of oxidation efficiency. As far as soil 1 is concerned it can be noticed that 3-CP (retention time: 16.5 min) is still present in case A (Fig. 8b), where complete oxidation is not achieved, whereas it is not detected in case E (Fig. 8c), where 3-CP is completely degraded after few minutes of reaction. By looking again at Fig. 8, it can be noticed that most peaks detected in samples A and E are also present in the blank sample (retention times: 14.1, 19.6, 20.3, 26.5 and 28.3 min) and thus cannot be attributed to oxidation byproducts. These are either impurities of the sample, or compounds purged by the column or SPME fiber coating. Uncomplete oxidation of chlorophenols may lead to the formation of different byproducts, such as chlorobenzendiols (molecular weight (MW) = 144), biphenyldiols (MW = 186), chlorodihydroxybiphenyls (MW = 220) and dichlorodihydroxybiphenyls (MW = 254) [24]. As shown in Fig. 8b and c, no major evidence of the presence of most of these compounds was obtained. Namely, the formation of 2,2′-dihydroxybiphenyl (MW = 186; retention time (r.t.) = 24.16 min) and of 2′-chloro-2,5-dihydroxybiphenyl (MW = 220; r.t. = 28.31 min), that were available from Sigma–Aldrich, could be absolutely excluded in sample E, whereas a small peak, probably corresponding to the latter one (MW = 220) was detected in sample E.

As shown in Fig. 9, a similar behavior was observed for soil 2; in this case, 3-CP was observed also in case E (Fig. 9c), since as reported in Fig. 5b, complete 3-CP oxidation is still not achieved after 3 h. Besides, the peak corresponding to 2′-chloro-2,5-dihydroxybiphenyl (MW = 220), detected in both samples A and E (see Fig. 9b and c) was observed also in the blank sample (Fig. 9a) and therefore could not be attributed to any oxidation byproduct. On the contrary, a very small peak, probably corresponding to a chlorodihydroxybiphenyl isomer (MW = 220; r.t. = 25.4) was detected in the sample E (Fig. 9c).

Nevertheless, from this analysis, it can be concluded that no major evidence of oxidation intermediates was observed in all tested conditions, thus indicating that great part of 3-CP is probably degraded to its final oxidation products, regardless of the operating conditions.

4. Conclusions

In this work it was shown that the efficiency of Fenton's and Fenton-like processes, usually assessed by monitoring the contaminant degradation in lab-scale experiments, may be correlated and somehow predicted through simple and fast hydrogen peroxide decomposition experiments. Hydrogen peroxide lifetime was effectively found to be rather well correlated to the contaminant oxidation efficiency allowing to build a reactivity scale where the higher oxidation efficiencies were assigned to the operating cases characterized by longer hydrogen peroxide lifetimes. The predictions of the reactivity scale were then confirmed by the results of 3-CP oxidation experiments, that generally resulted faster and more efficient whenever the predicted oxidation efficiency was higher. The proposed reactivity scale proved to be effective for comparing the different operating conditions for a single soil, but failed when used to compare the oxidation performances for different soils, since the different TOC content of the two soils, affecting both hydroxyl radicals scavenging and adsorptive behavior of the tested soils, may have influenced the space time yield of contaminant removal.

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References

[1] Decreto Ministeriale 471/99, Gazzetta Ufficiale della Repubblica Italiana 293, 1999.
[2] Y. Yin, H.E. Allen, In Situ Chemical Treatment, TE-99-10, GWRTAC, Pittsburgh, USA, 1999.
[3] R.L. Siegrist, M.A. Urynowicz, O.R. West, M.L. Crimi, K.S. Lowe, In Situ Chemical Oxidation Using Permanganate, Battelle Press, Columbus, OH, USA, 2001.
[4] S.J. Masten, S.H.R. Davies, J. Contam. Hydrol. 28 (1997) 327.
[5] M. Arienzo, J. Chiarenzelli, R. Scudato, J. Pagano, L. Falanga, Chemosphere 44 (2001) 1339.
[6] Q. Zhimin, C. Jih-Hsing, H. Chin-Pao, Water Res. 36 (2002) 85.
[7] G. Saracco, L. Solarino, V. Specchia, M. Maja, Chem. Eng. Sci. 56 (2001) 4.
[8] J. Walling, Acc. Chem. Res. 8 (1975) 125.
[9] R.J. Watts, M.D. Udell, P.A. Rauch, Hazard. Wastes Hazard. Mater. 7 (1990) 335.
[10] J.X. Ravikumar, M.D. Gurol, Environ. Sci. Technol. 28 (1994) 394.
[11] P.K.C. Kakarla, R.J. Watts, J. Environ. Eng. 123 (1997) 11.
[12] C.L. Ho, M.A.A. Shebl, R.J. Watts, Hazard. Wastes Hazard. Mater. 12 (1995) 15.
[13] R.J. Watts, M.D. Udell, R.M. Mansen, Water Environ. Res. 65 (1993) 839.
[14] C.M. Miller, R.L. Valentine, J. Hazard. Mater. 41 (1995) 105.
[15] R.J. Watts, M.K. Foget, S. Kong, A.L. Teel, J. Hazard. Mater. B 69 (1999) 229.
[16] M.E. Lindsey, M.A. Tarr, Chemosphere 41 (2000) 409.
[17] A. Walkey, I.A. Black, Soil Sci. 37 (1934) 29.
[18] A. Tessier, P.G.C. Campbell, M. Bisson, Anal. Chem. 51 (1979) 844.
[19] G.E.M. Hall, P. Pelchat, Water Air Soil Pollut. 112 (1999) 41.
[20] C.M. Miller, R.L. Valentine, Water Res. 33 (1999) 2805.
[21] R. Baciocchi, M.R. Boni, F. Lombardi, G. Lombardi, in: Proceedings of the 17th International Conference on Solid Waste Technology and Management, Philadelphia, PA, USA, 2001, p. 470.
[22] R. Baciocchi, M. Attin, G. Lombardi, M.R. Boni, J. Chromatogr. A 911 (2001) 135.
[23] W.C. Schumb, C.N. Sateerfield, R.L. Wentworth, Hydrogen Peroxide, ACS Monograph Series, Reinhold, New York, 1955, p. 557.
[24] A. Hirvonen, M. Trapido, J. Hentunen, J. Tarhanen, Chemosphere 41 (2000) 1211.