In situ oxidation remediation technologies: Kinetic of hydrogen peroxide decomposition on soil organic matter

Arturo Romero [a,*], Aurora Santos [a], Fernando Vicente [a], Sergio Rodriguez [a], A. Lopez Lafuente [b]

[a] Dpto Ingenieria Quimica, Facultad de Ciencias Químicas, Universidad Complutense Madrid. Ciudad Universitaria S/N. 28040 Madrid, Spain
[b] Dpto Edafología, Facultad de Farmacia, Universidad Complutense Madrid. Plaza Ramón y Cajal S/N. 28040 Madrid, Spain

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ABSTRACT

Rates of hydrogen peroxide decomposition were investigated in soils slurries. The interaction soil–hydrogen peroxide was studied using a slurry system at 20 °C and pH 7. To determine the role of soil organic matter (SOM) in the decomposition of hydrogen peroxide, several experiments were carried out with two soils with different SOM content (S1 = 15.1%, S2 = 10%). The influence of the oxidant dosage ($[H_2O_2]_o$ from 10 to 30 g L^{-1} and soil weight to liquid phase volume ratio = 500 g L^{-1}) was investigated using the two calcareous loamy sand soil samples. The results showed a rate dependency on both SOM and hydrogen peroxide concentration being the H_2O_2 decomposition rate over soil surface described by a second-order kinetic expression $r_{H_2O_2} = \frac{-dn_{H_2O_2}}{W_{SOM}dt} = kC_{H_2O_2}C_{SOM}$.

Thermogravimetric analysis (TGA) was used to evaluate the effect caused by the application of this oxidant on the SOM content. It was found a slightly increase of SOM content after treatment with hydrogen peroxide, probably due to the incorporation of oxygen from the oxidant (hydrogen peroxide).

1. Introduction

The contamination of soils remains a significant problem in recent years in Europe. In situ chemical oxidation (ISCO) shows current alternative for contaminated soils remediation. While many of the chemical oxidants have been used in wastewater treatment for decades, only recently they have been used to treat contaminated groundwater by hydrocarbon and soil in-situ. One of the chemical oxidation processes is the Fenton reaction, which uses H_2O_2 as oxidant and ferrous ions as catalyst to generate OH$^\bullet$. It is an interesting technology due to its high efficiency and low cost [1]. This oxidant may be capable of converting the hydrocarbon mass to carbon dioxide and water in sufficient contact time with organic contaminants. However, hydrogen peroxide stability is the primary limitation of the use of catalyzed hydrogen peroxide propagations for ISCO [2,3]

The use of hydrogen peroxide was once popular because it is relatively inexpensive, is non-persistent, and is unlikely to be a health hazard if is used properly. However, oxidation treatment may also have an effect on the soil. Oxidative processes initiated by OH$^\bullet$ could alter the nature and speciation of the organic and inorganic constituents within the soil [4]. The choice of appropriate technologies for soil remediation rarely takes into account the impact on soil [5].

Several works have appeared which emphasized the efficiency of Fenton processes for the remediation of contaminated soils with organic compounds [6–11]. However, few works have studied the interaction hydrogen peroxide-soil by using the Fenton process [1,5,12], with achieving diverse findings probably due to the differences among the soil type, soil organic matter (SOM) content and the method for SOM quantification. For example, Villa et al. [12] found that 80% of the organic matter naturally present on the soil was degraded while Sun and Yan [1] found an asymptotic value of 30% for this degradation. Sirguey et al. [5] found differences between SOM values before and after oxidation among 13% and 90%, depending on the soil and the oxidant used (permanganate and Fenton reagent). Bissey et al. [3] studied SOM–hydrogen peroxide dynamics with naturally-occurring soils minerals finding a 30% SOM decrease after treatment with H_2O_2 at acid pH (pH 3) while the SOM remained almost constant at neutral pH (pH 7).

On the other hand, it was noticed in literature that hydrogen peroxide is decomposed when it is in contact with the soil, even when uncontaminated soil is used [3,13]. Scarce information is given in literature about kinetic aspects of H_2O_2 decomposition rate. First order for hydrogen peroxide has been assumed [13] as was also found for hydrogen peroxide decomposition using not soil but iron oxides as solid phase [14,15].

The disappearing rate of the oxidant must be taking into account to establish the required dosage of hydrogen peroxide

Nomenclature

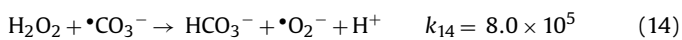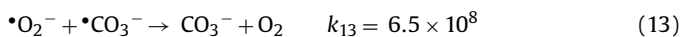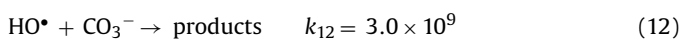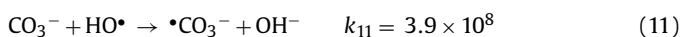|	
$C_{H_2O_2}$	hydrogen peroxide concentration $(g_{H_2O_2}\,L^{-1})$
C_{SOM}	soil organic matter concentration $(g_{SOM}\,g_{soil}^{-1})$
k	kinetic constant $(g_{soil}\,L\,g_{SOM}^{-2}\,min^{-1})$
$r_{H_2O_2}$	hydrogen peroxide decomposition rate $(g_{H_2O_2}\,g_{SOM}^{-1}\,min^{-1})$
SOM	soil organic matter (%)
SQR	weighted residual sum of squares $\sum\left(X_{exper}-X_{calculated}\right)^2$
T	temperature (°C)
TGA	thermogravimetric analysis
V_L	liquid phase volume (L)
W/V_L	soil weight to liquid phase volume ratio $(g_{soil}\,L^{-1})$
W_{SOM}	weight of soil organic matter (g_{SOM})
$(X_{H_2O_2})$	hydrogen peroxide conversion (%)

Greek symbol

ν	empiric stoichiometric coefficient $(g_{SOM}\,g_{soil}^{-1})\left(g_{H_2O_2}\,L^{-1}\right)^{-1}$

in the treatment of soils. Both SOM and organic pollutant can compete for the hydrogen peroxide. Moreover, the SOM naturally contained is usually much higher than the pollutant content and consequently SOM could have a strong influence on the required hydrogen peroxide dosage for soil remediation. Therefore, the oxidant must be added in an amount enough to assure the contaminant degradation in the presence of the natural SOM.

The amount of hydrogen peroxide needed to degrade a given concentration of contaminant in soil is often far greater than in aqueous systems. If the soil contains appreciable SOM, the required H_2O_2/contaminant molar ratios can be in the order of 10^2–10^3 [16].

The reactivity of the hydrogen peroxide once H_2O_2 and soil are mixed can be attributed to several reactions taking place simultaneously. Some of the most relevant reactions and rate constant at 20–25 °C in the literature are below [17,18]:

$$H_2O_2 \rightarrow 2HO^\bullet \qquad k_1 = 8 \times 10^{-9} \tag{1}$$

$$H_2O_2 + O_2 \rightarrow 2HO_2^\bullet \qquad k_2 = 1.3 \times 10^{-19} \tag{2}$$

$$H_2O_2 + HO^\bullet \rightarrow H_2O + HO_2^\bullet \qquad k_3 = 2.7 \times 10^{-7} \tag{3}$$

$$HO^\bullet + O_2^{-\bullet} \rightarrow HO_2^- + O_2 \qquad k_4 = 9.7 \times 10^{-7} \tag{4}$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad k_5 = 3.1 \times 10^6 \tag{5}$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad k_6 = 1.3 \times 10^{36} \tag{6}$$

$$H_2O + O_2 \rightarrow HO_2^\bullet + HO^\bullet \qquad k_7 = 5.4 \times 10^{-41} \tag{7}$$

$$SOM + HO^\bullet \rightarrow products \qquad k_8 = 10^7 - 10^{10} \tag{8}$$

$$CaCO_{3(s)} + H^+ \leftrightarrow Ca^{2+} + HCO_3^- \qquad K = 269 \tag{9}$$

$$HCO_3^- + HO^\bullet \rightarrow {}^\bullet CO_3^- + H_2O \qquad k_{10} = 8.5 \times 10^6 \tag{10}$$

$$CO_3^- + HO^\bullet \rightarrow {}^\bullet CO_3^- + OH^- \qquad k_{11} = 3.9 \times 10^8 \tag{11}$$

$$HO^\bullet + CO_3^- \rightarrow products \qquad k_{12} = 3.0 \times 10^9 \tag{12}$$

$${}^\bullet O_2^- + {}^\bullet CO_3^- \rightarrow CO_3^- + O_2 \qquad k_{13} = 6.5 \times 10^8 \tag{13}$$

$$H_2O_2 + {}^\bullet CO_3^- \rightarrow HCO_3^- + {}^\bullet O_2^- + H^+ \qquad k_{14} = 8.0 \times 10^5 \tag{14}$$

$$HO_2^- + {}^\bullet CO_3^- \rightarrow HCO_3^- + {}^\bullet O_2^- \qquad k_{15} = 3.0 \times 10^7 \tag{15}$$
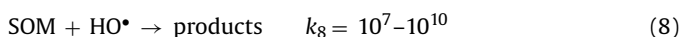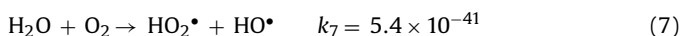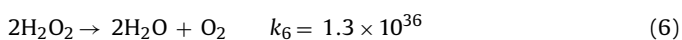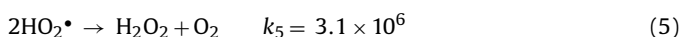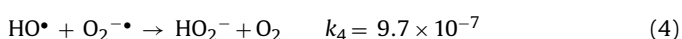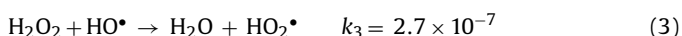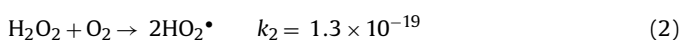
Although hydroxyl radicals, hydroperoxyl radicals, hydrogen peroxide and oxygen are all oxidants, hydroxyl radicals have the

Table 1
Properties of the soils samples.

Soil	Texture	pH in water	SOM $(g_{SOM}\,g_{soil}^{-1})$ 100	Equiv. $CaCO_3$ (%)
S1	Loamy sand	7.4	15.1	10.7
S2		7.8	10	7.3

strongest oxidation capability, and are considered responsible for oxidizing organic compounds [19].

The objective of the present paper is to research the kinetics and mechanism of H_2O_2 decomposition on soils at natural neutral pH. The oxidant agent (hydrogen peroxide) concentration and SOM content have been examined. The soils were calcareous throughout their thickness. Such little studied soils are abundant throughout the Mediterranean Basin and in Spain.

2. Materials and methods

2.1. Reagents

Hydrogen peroxide 30% (w/w) from Riedel de Haën was used in the degradation experiments. Titanium(IV) oxysulphate solution from Riedel de Haën was used in the determination of hydrogen peroxide. All of the suspensions and solutions were prepared with Milli-Q water (>18 MΩ cm) purified with a deionizing system.

2.2. Soil samples

The soils selected for this study (S1 and S2) were categorized as loamy sand at neutral pH. The main difference between the two soil samples was the SOM content. The properties of S1 and S2 are shown in Table 1. The soils were classified as calcaric Fluvisols (FLca). This is a type of soil that develops the basins of the main rivers that traverse limestone material, which is the dominant material in the eastern half of the Iberian Peninsula [20].

The pH was measured in 1:2.5 soil/water suspensions [21]. The $CaCO_3$ equivalent was determined by calcimeter Bernard method. The SOM content in the soils was determined by thermogravimetric analysis (TGA), as described in Section 2.4.

The SOM present in the soils S1 and S2 has also been burned by incineration of a known weight of sample placed in a ceramic crucible in an electric muffle for 2 h at 550 °C obtaining the corresponding SOM content by mass difference.

2.3. Experimental conditions of hydrogen peroxide decomposition

Kinetic for hydrogen peroxide degradation was studied for each soil through batch experiments, performed in vials, kept in continuous agitation (50 rpm) on a shaking water bath UNITRONIC, supplied by SELECTA The temperature was controlled, and continuously monitored during the experiments and remained always at

Table 2
Operating conditions of H_2O_2 decomposition for runs carried out in batch tests. $T = 20$ °C; $W/V_L = 500$ g L^{-1}; $u = 50$ rpm.

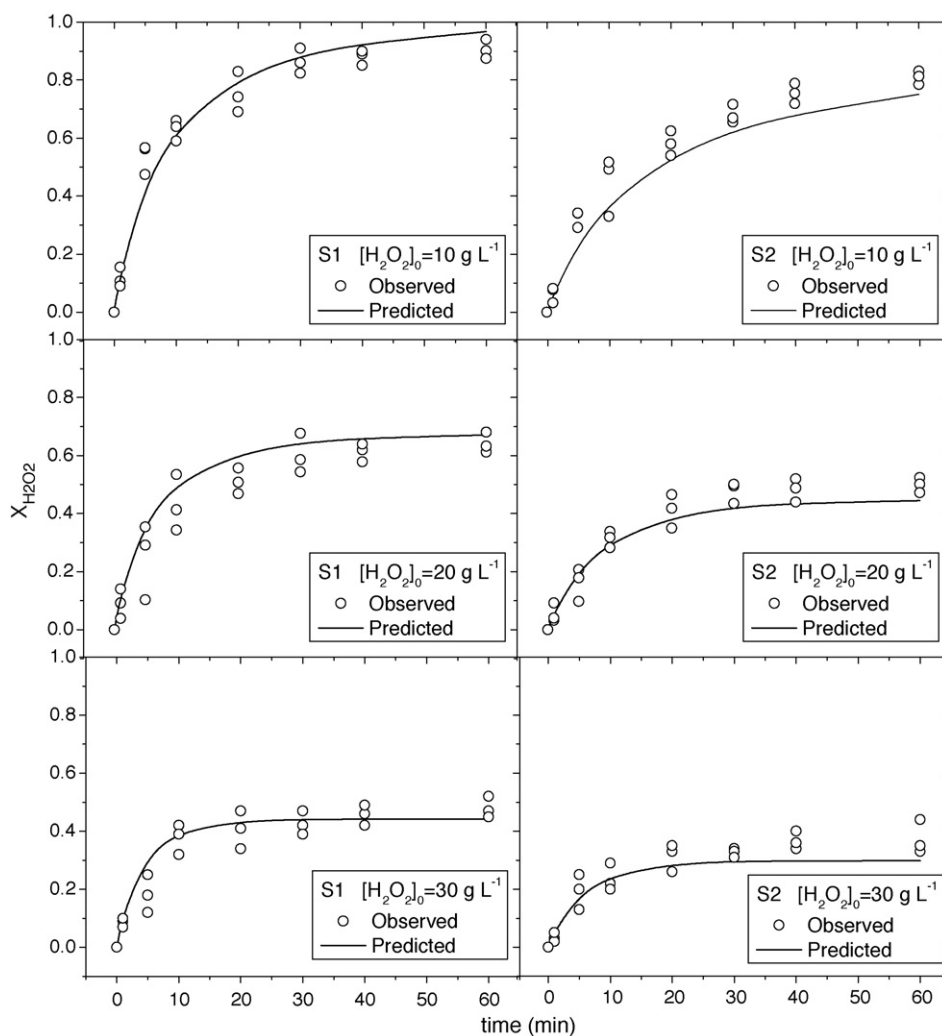| RUN	Soil	$[H_2O_2]_0$ $(g\,L^{-1})$	Initial H_2O_2 dosage $\left(mg_{H_2O_2}\,g_{soil}^{-1}\right)$	Initial H_2O_2 dosage $\left(mg_{H_2O_2}\,g_{SOM}^{-1}\right)$
1	S1	10	20	132
2	S1	20	40	265
3	S1	30	60	397
4	S2	10	20	200
5	S2	20	40	400
6	S2	30	60	600
7	S1	20	40	SOM loss by ignition
8	S2	20	40	

Fig. 1. Experimental (symbols) and predicted (lines) $\left(X_{H_2O_2}\right)$ vs. time values obtained in the decomposition of hydrogen peroxide by soil samples S1 and S2.

20 °C. The uncontaminated soil weight to liquid phase volume ratio (W/V_L) was 500 g L^{-1}. The experiments were carried out at different initial concentrations of hydrogen peroxide (10, 20 and 30 g L^{-1}). The soil pH was not adjusted. In order to avoid possible explosions due to gas accumulation in the vials, the caps were not sealed during reaction time to permit evacuation of the generated gas [22]. The samples were collected at different reaction times and immediately centrifuged for 5 min in a CENTROLIT SELECTA centrifuge. After centrifugation, the supernatant was analyzed for hydrogen peroxide, as

described below. Repeating the same batch experiment by sampling at different reaction times (0–1–5–10–20–30–40–60 min) allowed to obtain the kinetics of hydrogen peroxide decomposition. These experiments were performed by triplicate.

The experiments conducted to separate SOM effect in the hydrogen peroxide stability have been performed in the same operational conditions with the two soil samples in which the removal of SOM fraction content by incineration has been achieved (runs 7–8 in Table 2).
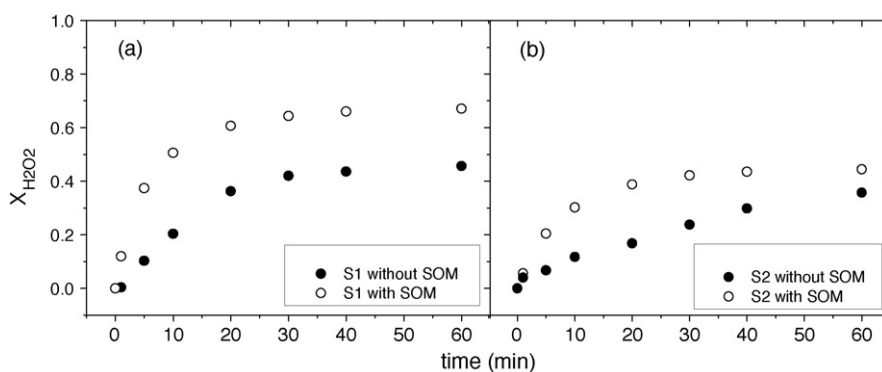

Fig. 2. Conversion of H$_2$O$_2$ on the soils S1 (a) and S2 (b) with and without SOM. [H$_2$O$_2$]$_o$ 20 g L^{-1}.

2.4. Analytical methods

Hydrogen peroxide concentration in the supernatant was measured using a UV-1603 spectrophotometer, supplied by Shimadzu, after colour development with titanium sulphate technique [23].

Thermogravimetric measurements were carried out in a module of simultaneous thermal analysis TGA/STDA 851 (Mettler Instruments). The SOM was determined by the mass loss in the interval from 150 to 550 °C in the thermogravimetric curve. The sample was heated in an alumina crucible. During thermogravimetric analysis, about 13 mg of the samples were first heated in the thermo-balance in a flow of atmosphere air (20 mL min^{-1}) at a rate of 20 °C min^{-1} up to 550 °C. Sequently, the samples were isothermally heated at 550 °C for 2 h.

3. Results and discussion

3.1. Hydrogen peroxide decomposition

Hydrogen peroxide decomposition, without pH adjustment, was measured in order to characterize the reactivity of the selected soils. Hydrogen peroxide concentrations were monitored with time at two values of SOM content (S1, S2) and three values of initial H_2O_2 concentration (10, 20 and 30 g L^{-1}) In Fig. 1 the hydrogen peroxide consumed $\left(X_{H_2O_2}\right)$ vs. time is shown.

The data in Fig. 1 indicate that, for the same value of the initial H_2O_2 concentration, higher hydrogen peroxide decomposition is obtained if the concentration of SOM increases. Under neutral pH conditions, hydrogen peroxide is decomposed more slowly in S2 (SOM = 10%) than in S1 (SOM = 15.1%).

On the other hand, it can be pointed out from Fig. 1 that asymptotic values for hydrogen peroxide decomposition are reached. For a given soil, the value of this asymptote increases as the initial H_2O_2 dosage does. This fact, not previously described in literature, could be explained if the compounds reacting with the hydrogen peroxide are totally oxidized before this oxidant is fully consumed.

The asymptote in the H_2O_2 decomposition was not found for acidic pH and using iron species (added or naturally occurring in soils) [3]. This could be explained because at these conditions, the hydrogen peroxide decomposition occurs by a different mechanism that at neutral pH.

In Fig. 2 are shown the hydrogen peroxide consumptions in contact with S1 and S2 at $[H_2O_2]_0 = 20$ g L^{-1}. They are compared to consumption of soil samples with SOM loss by ignition at the same hydrogen peroxide concentration (runs 2–5–7–8 in Table 2). The hydrogen peroxide decomposition is more slowly when the SOM content is throughout removed by ignition. Low asymptotic conversion is obtained with calcinated soils

Data shown in Fig. 2 indicate for each soil that the H_2O_2 is decomposed also by the inorganic matter. Moreover, it can be supposed that the main contribution to the hydrogen peroxide decomposition could be related to the soil carbonate content. In fact, soil S2 has a lower CaCO$_3$ content (7.3%) than S1 and lowered H_2O_2 consumption is obtained for the incinerated soil S2, as shown in Fig. 2b. However, data obtained with soils S1 and S2 before and after calcination should be carefully compared while the SOM can strongly modify the accessibility and interaction of the hydrogen peroxide to the mineral surface. Therefore, the contribution of the SOM to the hydrogen peroxide decomposition can not be analyzed as the difference obtained before and after calcination.

3.2. Change of SOM content after oxidation

In Fig. 3, weight changes by TGA measurements before and after treatment ($t = 60$ min) of soils used in runs 2 and 5 in Table 2 are
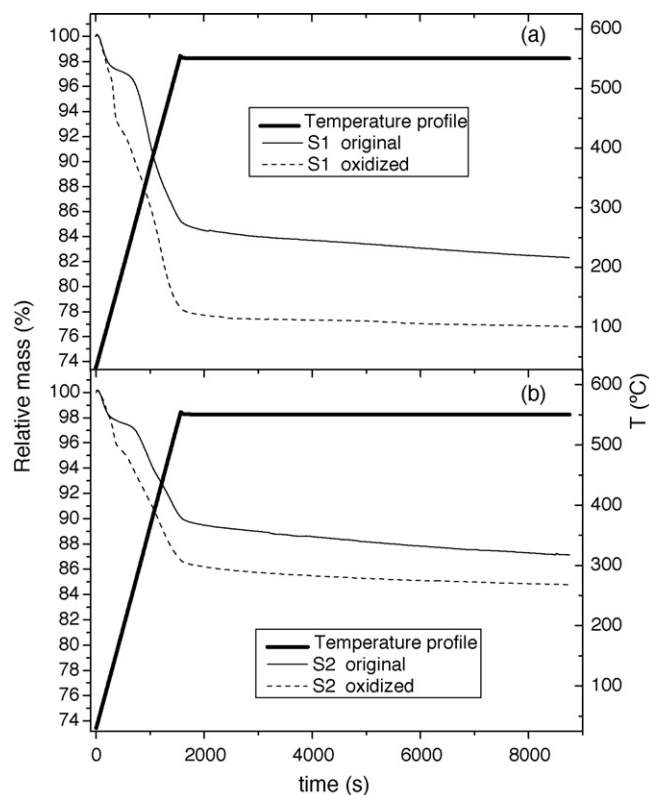

Fig. 3. Relative mass loss by TGA of the soils S1 (a) and S2 (b) with and without H_2O_2 treatment. Reaction time = 60 min, $[H_2O_2]_0 = 20$ g L^{-1}.

shown ($[H_2O_2]_0 = 20$ g L^{-1}). The SOM initial and by treatment with hydrogen peroxide has been calculated from the relative mass difference between 150 and 550 °C in the two curves obtained with each soil (Fig. 3a and b). It has been obtained that the SOM initially present in soil S1 changes from 151 to 164 mg$_{SOM}$ g$_{soil}$$^{-1}$, being changes for S2 from 100 to 113 mg$_{SOM}$ g$_{soil}$$^{-1}$ Therefore, the total SOM content is slightly modified after oxidation. These results are consistent with the data obtained by incineration: S1 changes from 155 to 173 mg$_{SOM}$ g$_{soil}$$^{-1}$ and S2 changes from 91 to 98 mg$_{SOM}$ g$_{soil}$$^{-1}$. This weak weight increase could be attributed to the oxygen introduced by the oxidation of the original SOM. The SOM is then oxidized but not mineralized.

Therefore, having into account the results from TGA and the asymptotic values for hydrogen peroxide decomposition in Fig. 1 the following reaction is proposed to describe the oxidation of the SOM and decomposition of hydrogen peroxide:

$$H_2O_2 + \nu SOM \rightarrow SOM_{OX} + Products \qquad (16)$$
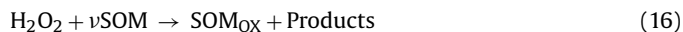
Moreover, Eq. (16) describing the decomposition of hydrogen peroxide by SOM could be derived if some of the radical reactions in Eqs. (1)–(15) are lumped (i.e. Eqs. (1) and (8)). An empirical stoichiometric coefficient ν is used to do this.

To explain the asymptotic value of hydrogen peroxide conversion in Fig. 1 the SOM in the Eq. (16) could acts as limiting reagent. When the SOM surface sites are exhausted, the hydrogen peroxide is not more decomposed and reaches a constant value.

3.3. Decomposition kinetic of H_2O_2

The data of the runs conducted in the batch system at pH 7 in the presence of 0.5 g of soil samples presented in Fig. 1 were used to discriminate the kinetic model. According to Eq. (16), not only the H_2O_2 but also the SOM must be included in the kinetic equation

Table 3
Parameters values estimated by fitting data obtained in the hydrogen peroxide decomposition in soils S1 and S2 separately. $[k] = (g_{soil} \, L \, g_{SOM}^{-2} \, min^{-1})$ $[\nu] = \left(g_{SOM} \, g_{soil}^{-1} \right) \left(g_{H_2O_2} \, L^{-1} \right)^{-1}$.

Experimental data fitting	Parameter	Value	Standard error	Confidence interval	SQR
Runs 1, 2 and 3	k	1.07×10^{-2}	7.19×10^{-4}	1.21×10^{-2}	2.96×10^{-1}
	υ	1.19×10^{-2}	3.59×10^{-4}	1.26×10^{-2}	
Runs 4, 5 and 6	k	1.39×10^{-2}	6.85×10^{-4}	1.53×10^{-2}	1.31×10^{-1}
	υ	0.84×10^{-3}	2.59×10^{-4}	1.03×10^{-2}	

Table 4
Parameters values estimated by fitting data obtained in the hydrogen peroxide decomposition in soils S1 and S2 simultaneously. $[k] = (g_{soil} \, L \, g_{SOM}^{-2} \, min^{-1})$ $[\nu] = \left(g_{SOM} \, g_{soil}^{-1} \right) \left(g_{H_2O_2} \, L^{-1} \right)^{-1}$.

Experimental data fitting	Parameter	Value	Standard error	Confidence interval	SQR
Runs with S1 and S2	k	1.24×10^{-2}	6.35×10^{-4}	1.41×10^{-2}	6.05×10^{-1}
	υ	1.11×10^{-2}	2.64×10^{-4}	1.20×10^{-2}	

and the asymptotic values in Fig. 1 must be explained. To do this, the following second-order kinetics expression is proposed:

$$\frac{-dn_{H_2O_2}}{W_{SOM}dt} = r_{H_2O_2} = kC_{H_2O_2}C_{SOM} \tag{17}$$

where k is the kinetic constant, C_{SOM} and $C_{H_2O_2}$ are the SOM concentration and the hydrogen peroxide concentration, respectively; and the parameter W_{SOM} is the organic matter mass initially contained for each soil. In Eq. (17) it is supposed that hydrogen peroxide decomposition occurs in a heterogeneous way as was previously found elsewhere [24]. Moreover, blank runs for hydrogen peroxide decomposition carried out at neutral pH in absence of soil show a negligible decomposition of the hydrogen peroxide and confirm the heterogeneous mechanism.

By introducing the organic slurry density, W_{SOM}/V_L, in Eq. (17) the following expression is obtained:

$$\frac{-dC_{H_2O_2}}{dt} = k\frac{W_{SOM}}{V_L}C_{H_2O_2o}(1 - X_{H_2O_2})C_{SOM} \tag{18}$$

Having into account Eq. (16) the stoichiometric relationship between C_{SOM} and $C_{H_2O_2}$ results:

$$C_{SOM} = C_{SOMo} - \nu C_{H_2O_2o} X_{H_2O_2} \tag{19}$$

being ν and empirical stoichiometric coefficient.

By introducing Eq. (19) in Eq. (18) the following expression is obtained:

$$\frac{dX_{H_2O_2}}{dt} = k\frac{W_{SOM}}{V_L}C_{H_2O_2o}(1 - X_{H_2O_2})\left(\frac{C_{SOMo}}{C_{H_2O_2o}} - \nu X_{H_2O_2} \right) \tag{20}$$

The collected experimental $\left(X_{H_2O_2} \right)$ vs. time curves were fitted to Eq. (20). Non linear regression by using a Marquardt algorithm has been applied in the fitting procedure. First, kinetic constants k and stoichiometric parameter υ have been estimated fitting each soil separately and parameters values obtained for soils S1 and S2 are summarized in Table 3. Residual sum of squares (SQR) for each soil have been calculated by comparison of experimental data to those predicted by the corresponding kinetic model. Standard deviation and confidence interval values of the estimated parameters are also provided in Table 3. As can be seen a satisfactory fitting is obtained.

As deduced from Table 3 the k and υ values obtained for each soil are quite similar, validating the approach in Eq. (20). Therefore, data obtained by using S1 and S2 have been simultaneously fitted to Eq. (20) and the estimated and statistical parameters values obtained are summarized in Table 4. Predicted $\left(X_{H_2O_2} \right)$ using the estimated parameters from Table 4 are shown as lines in Fig. 1. As is shown in Fig. 1, the experimental and simulated data are plotted as points

and lines, respectively. As can be seen, even using a unique kinetic parameters for the different soils and hydrogen concentration used, a good agreement is noticed in all cases, for the whole initial hydrogen peroxide concentration interval used ($10–30 \, g \, L^{-1}$) and for both soils (S1 and S2). Therefore, the kinetic model in Eq. (18) with the stoichiometric relationship in Eq. (19) is able to explain quite well the data obtained.

4. Conclusions

Soil slurries were investigated for hydrogen peroxide decomposition at neutral pH. Soils with higher SOM content increased the hydrogen peroxide decomposition rate. Moreover, a slight SOM increase was found for S1 and S2 before and after the treatment. It could be due to the introduction of oxygen in the original SOM creating oxidized surface sites. This fact, together with the asymptotic values found for the hydrogen peroxide conversion, could be explained by using the second-order kinetic model here proposed. The SOM reacts with the hydrogen peroxide being totally oxidized (not mineralized) before this oxidant is fully consumed at the conditions tested. The hydrogen peroxide decomposition was observed to follow a second-order kinetic. A kinetic constant around $1.24 \times 10^{-2} \, g_{soil} \, L \, g_{SOM}^{-2} \, min^{-1}$ was found. The empiric stoichiometric coefficient used to relate the SOM and hydrogen peroxide changes, ν, was estimated by data fitting as $0.0111 \left(g_{SOM} \, g_{soil}^{-1} \right) \left(g_{H_2O_2} \, L^{-1} \right)^{-1}$.

On the other hand, the results of this research show that hydrogen peroxide as oxidant reagent for in situ remediation does not significantly change the SOM total content although could modified its oxidation state.

The high concentrations of hydrogen peroxide requirements found in literature for in situ oxidation of sorbed contaminants by modified Fenton's reagent could be related to the SOM-hydrogen peroxide interaction consuming this reactant.

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