



Chemical oxidation of 2,4-dimethylphenol in soil by heterogeneous Fenton process

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ARTICLE INFO

Article history:

Received 12 March 2008
Received in revised form 9 May 2008
Accepted 20 May 2008
Available online 29 May 2008

Keywords:

Fenton's reagent
Soil remediation
Chelating agent
Neutral pH
2,4-Dimethylphenol

ABSTRACT

Hydrogen peroxide has been used to oxidize a sorbed aromatic contaminant in a loamy sand with 195.9 g kg^{-1} of organic carbon by using iron as catalyst at 20°C . The 2,4-dimethylphenol (2,4-DMP) was chosen as pollutant. Because of this soil generates a slightly basic pH in contact to an aqueous phase the solubility of the iron cation was determined in absence and presence of a chelating agent (L-ascorbic acid, L-Asc) and with and without soil. From results, it was found that in presence of soil the iron cation was always adsorbed or precipitated onto the soil. Therefore, the procedure selected for soil remediation was to add firstly the iron solution used as catalyst and following the hydrogen peroxide solution used as oxidant. As iron cation is sorbed onto the soil before the oxidant reagent is provided a heterogeneous catalytic system results.

This modified Fenton runs have been carried out using $0.11 \text{ mg}_{2,4\text{-DMP}} \text{ g}^{-1} \text{ soil}$ and $2.1 \text{ mg}_{\text{Fe}} \text{ g}^{-1} \text{ soil}$. The H_2O_2 /pollutant weight ratios used were 182 and 364. The results show that H_2O_2 oxidizes 2,4-DMP producing CO_2 and acetic acid. After 20 min of reaction time a pollutant conversion of 75% and 86% was found, depending on the H_2O_2 dosage.

Moreover, it was found that hydrogen peroxide was heterogeneously decomposed by the soil (due to its organic and/or inorganic components) and its decomposition rate decreases when the iron was previously precipitated-impregnated into the soil.

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1. Introduction

The remediation of contaminated soils is becoming a problem of increasing importance. Standard technologies (pump and treat at the surface) are known to be expensive and to take years to complete. Soils contaminated with hydrocarbons (petroleum residues, solvents, pesticides, wood preservatives, etc.) present one of the most difficult challenges for remediation specialists. In situ chemical oxidation is a developing class of remediation technologies in which organic contaminants are degraded in place by oxidants delivered to the surface. Among these, Fenton's Reagent seems to be a promising one and the number of studies on this topic is increasing in the last years [1–3].

Based on the successful results obtained in the treatment of aqueous wastes, catalyzed H_2O_2 has been applied to the remediation of contaminated soils [4–6]. Hydrogen peroxide is particularly effective when it reacts with ferrous iron (Fe^{2+}) to produce Fenton's

reagent. Acidic pH has been often used to optimize Fenton oxidation efficiency in aqueous phase [7]. However, the pH of many soils is often near neutral or slightly alkaline and acidic soil environments might cause dramatic ecological impacts.

Because of this soil pH it is noticed that the Fe^{2+} quickly precipitates disappearing from the aqueous phase. To maintain soluble iron, chelating agents have been used employing Fe^{3+} as catalytic specie in a Fenton-like process [8]. On the other hand, naturally occurring iron minerals have been successfully used in a heterogeneous Fenton process [9]. These results indicate that iron minerals can serve as catalysts for Fenton-like reactions in place of soluble iron, raising the possibility of in situ Fenton-like treatment of contaminated soils without pH adjustment. Although Fenton oxidation at natural soil pH has been shown to be less efficient, several studies have shown that degradation was still feasible [10,11]. A greater production rate of HO^\bullet was reported in the H_2O_2 /iron oxyhydroxide system at natural pH [12].

It has been also found a remarkable instability of hydrogen peroxide for many types of soils. When this oxidant gets in touch with inorganic compounds, such as iron oxyhydroxides and manganese oxyhydroxides catalysts, or with organic compounds commonly found in surface soils, it can quickly decompose. Consequently, an

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excess amount of hydrogen peroxide is usually required [13]. An excess concentration of hydrogen peroxide enhances the destruction of highly hydrophobic contaminants [14]. Vigorous Fenton-like reactions using high concentrations of H_2O_2 generate nonhydroxyl radical species, such as superoxide radical ($\text{O}_2^{\bullet-}$) and hydroperoxide anion (HO_2^-), which are reductants and nucleophiles that seem to be responsible of the rapid treatment of sorbed and nonaqueous-phase liquid (NAPL) contaminants relative to natural rates of desorption and dissolution [15].

Some contaminants in soils exist as particulate and sorbed conditions, and a strong oxidizing condition is required to degrade contaminant efficiently. The purpose of this study is to investigate the application of catalyzed hydrogen peroxide for oxidizing sorbed contaminants. The 2,4-dimethylphenol (2,4-DMP) was tested as a model phenolic pollutant because of its high toxicity and low vapor pressure. The soil selected for the present study was classified as loamy sand with 195.9 g kg^{-1} of organic carbon (OC). This high amount of OC produces a strong sorption of the selected pollutant 2,4-DMP [16]. Iron is initially added to the contaminated soil thus resulting in a heterogeneous catalyst. H_2O_2 decomposition and oxidation of the pollutant sorbed in soil by the remaining H_2O_2 has been analyzed.

2. Materials and methods

2.1. Reagents

Hydrogen peroxide (30%), iron (Fe(II)) sulphate, iron (Fe(III)) sulphate (75%), L-ascorbic acid (L-Asc, 99%), sodium carbonate anhydrous, sodium hydrogen carbonate, 2,4-dimethylphenol (2,4-DMP, 98%), methanol used as solvent for pollutant extraction, titanium(IV) oxysulphate solution for the determination of peroxides, *o*-cresol (99+%) used as internal standard for gas chromatography-flame ionization detection (GC-FID) analysis, formic acid (85%) used as internal standard for acids measured. All of the suspensions and solutions were prepared with Milli-Q water ($>18 \text{ m}\Omega \text{ cm}$) purified with a deionizing system.

2.2. Characterization of soil samples

The soil selected for the present study was calcareous throughout their depth, a typical feature of the Mediterranean region [17]. The soil studied was categorized as loamy sand with various characteristics listed in Table 1.

Analytical parameters were determined according to ISRIC [18]. Organic carbon was quantified by wet oxidation according to Walkley–Black [19]. Total nitrogen was determined using the Kjeldahl method [20]. The pH was measured in 1:2.5 soil/water suspension [18]. The CO_3Ca equivalent was determined using a Bernard calcimeter. Electrical conductivity was measured in a 1:5 soil/water suspension [18]. Cation exchange capacity was determined by extracting samples with 1 M ammonium acetate at pH 7.0 [21], exchange cations being quantified by atomic absorption spectroscopy (Ca and Mg) or flame emission spectrometry (Na and K).

Table 1
Physical and chemical properties of soil samples

Texture	pH in water	EC ($\mu\text{S cm}^{-1}$)	CO_3Ca (%)	Organic C (g g^{-1})	Total N (g kg^{-1})	CEC	Exchanged bases (cmol kg^{-1})			
							Ca^{2+}	Mg^{2+}	Na^+	K^+
Loamy sand	7.4	471	10.7	0.1959	6.2	26.10	13.19	3.08	0.28	0.09

EC: electrical conductivity; CEC: cation exchange capacity.

2.3. Precipitated–impregnated iron

Fe(II) was added as ferrous sulphate in aqueous solution. Experiments were conducted in a water bath at 20°C and 120 rpm. In batch system on 1 g soil samples and 2 mL of SO_4Fe solution in 20 mL glass vials. Liquid–solid separation was done by centrifugation. To determine the amounts of precipitated–impregnated iron in the soil, aqueous metal concentrations were measured. The iron concentration in soil was determined from a mass balance on Fe(II) in the liquid phase.

Previously, in the same operation conditions, the stability of Fe^{3+} was also tested with an initial concentration of 1000 mg L^{-1} in alkaline aqueous phase (pH about 10 by adding CO_3Na_2) and in soil slurries (1:2 soil/water suspension) by adding L-Asc as a metal chelating agent in a mass ratio L-Asc/ Fe^{3+} : 0.8, 1.6 and 3.2.

2.4. Adsorption 2,4-DMP tests

Adsorption equilibrium experiments were performed in 40 mL amber glass vials capped with Teflon faced silicon septa. A 10 g soil sample uncontaminated soil was added to the vial, together with 35 mL of a 2,4-DMP solution (initial concentration in the range $25\text{--}100 \text{ mg L}^{-1}$). To obtain the equilibrium the samples were shaken at room temperature (25°C) at 150 rpm for about 48 h [16]. The supernatant was analyzed for 2,4-DMP by gas chromatography, providing the 2,4-DMP equilibrium concentration in the liquid phase. The 2,4-DMP concentration in adsorbed phase was determined from a mass balance on 2,4-DMP in the liquid phase.

2.5. Hydrogen peroxide decomposition

The batch experiments were conducted in order to identify the variables responsible of the decomposition of hydrogen peroxide, e.g., iron and organic content of the soil.

Hydrogen peroxide degradation was studied through batch experiments, performed in 20 mL glass vials, kept in continuous agitation (120 rpm) on a shaking water bath SW22, supplied by Julabo. The temperature was controlled, and continuously monitored during the experiment and remained always in 20°C . The uncontaminated soil weight to liquid phase volume ratio (W/V_l) was changed from 1 to 0.25 g mL^{-1} . The experiments were carried out at different initial concentrations of hydrogen peroxide ($1000\text{--}25,000 \text{ mg L}^{-1}$). The samples were collected at different reaction times an immediately centrifuged for 5 min in a CENTROLIT SELECTA centrifuge. After centrifugation, the supernatant was analyzed for hydrogen peroxide, as described below.

2.6. Oxidation conditions

The 2,4-DMP oxidation experiments were performed in the same operating conditions used for the hydrogen peroxide experiments. The treatment was conducted in batch on 1 g 2,4-DMP contaminated soil sample with precipitated–impregnated Fe(II) in 20 mL glass vials. The Fenton-type reactions were started adding 2 mL H_2O_2 (initial concentration = $10,000\text{--}20,000 \text{ mg L}^{-1}$). Vials were examined at 0 and 20 min. Each reaction vial represents one

time point. 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 soil and aqueous phase were separated before the extraction. After centrifugation, both soil and supernatant were analyzed for 2,4-DMP. Ecotoxicity of the aqueous phase was measured by using the Microtox[®] bioassay. The iron content in the supernatant was also measured.

Potential toxic oxidation intermediates from 2,4-DMP adsorbed on the soil (1 g) were measured by extraction with Milli-Q water (5 mL). The vials were then placed on an ultrasonic bath for 1 h followed by centrifugation for 5 min. The supernatant fluid was then analyzed by using the Microtox[®] bioassay. The extracted 2,4-DMP from soil was also measured by GC in the aqueous phase obtained after sonication and centrifugation steps.

The total residual mass of the contaminant in the soil was extracted with methanol. The supernatant fluid was then analyzed for 2,4-DMP by means of a gas chromatograph (GC).

2.7. Analytical methods

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

Soluble iron concentrations were analyzed using a DR/890 colorimeter with the FerroVer Iron Reagent, supplied by HACH. Some samples were measured by ICP-AES and similar values were obtained validating the colorimetric method used.

Residual 2,4-DMP in the supernatant was analyzed by a Agilent Technologies 6890 N gas chromatograph, fitted with a flame ionization detector and equipped with a HP5 high resolution chromatography column (30 m length × 0.32 mm i.d.). The chromatographic conditions were initial oven temperature 110 °C, final oven temperature 135 °C, program rate 5 °C min⁻¹, injector temperature 300 °C, detector temperature 250 °C, and nitrogen carrier gas flow rate 25 mL min⁻¹.

To extract quantitatively the 2,4-DMP from the soil an ultrasonic solvent extraction were performed by 4 consecutive extractions. Each step accurately weighed spiked soil was sonicated 15 min with methanol in an ultrasonic bath (PowerSonic 505) at room temperature followed by a 5 min centrifugation. The relation soil/methanol was 1/5 (g mL⁻¹). The amount of total extracted 2,4-DMP was determined by GC.

The organic acid byproducts in both the supernatant and in the liquid phase of the extraction procedure after Fenton's runs were analyzed by ionic chromatography (Metrohm, mod. 761 Compact IC) using a conductivity detector; a column of anion suppression Metrosep ASUPP5 (25 cm length × 4 mm i.d.) was used as the stationary phase and an aqueous solution of 3.2 mM CO₃Na₂ and a 1 mM HCO₃Na as the mobile phase, at a constant flow rate of 0.7 mL min⁻¹.

After the Fenton runs, the Microtox[®] bioassay was used to determine the ecotoxicity of the supernatant. Moreover, to force desorption of potential toxic oxidation intermediates adsorbed onto the soil, sonication during 1 h of soil (1 g) with 5 mL of Milli-Q water and further centrifugation (5 min) was carried out and the ecotoxicity of the aqueous phase measured.

The Microtox bioassay is based on the decrease of light emission by *Photobacterium phosphoreum* resulting from its exposure to a toxicant, using a Microtox[®] M500 Analyzer (Azur Environmental). The inhibition of the light emitted by the bacteria was measured after 15 min contact time. The EC₅₀ is defined as the effective nominal concentration of toxicant (mg L⁻¹) that reduces the intensity of light emission by 50%. The parameter IC₅₀ is defined as the percentage of the initial volume of the sample to the volume of the sample yielding, after the required dilution, a 50% reduction of

the light emitted by the micro-organisms. The toxicity units of the wastewater are calculated as:

$$TUs = \frac{100}{IC_{50}} \quad (1)$$

Before measuring the toxicity, the pH values of all the samples were re-adjusted to between 6 and 7, in order to prevent the pH effect. All the chemicals used were purchased from Sigma-Aldrich and the micro-organisms were Microtox[®] Acute Reagent supplied by I.O. Analytical.

3. Results and discussion

3.1. Iron precipitated–impregnated tests

To maintain the soluble iron content is difficult due to its precipitation at neutral-pH. To avoid it the role of L-Asc was examined as metal chelating. In the carbonate solution free of soil (1000 mg L⁻¹ of CO₃Na₂) the ferric iron is maintained in aqueous solution by using L-Asc (Fig. 1). Therefore, the Fe(III) is stabilized when complexed with the L-Asc for the three mass ratio: 0.8, 1.6 and 3.2. Without chelating agent, both ferrous and ferric iron precipitated in these operation conditions. The final pH value in all these experiments free of soil were closed to neutral pH.

When the chelating agent was added to the water–soil slurries, it was not capable of maintaining the Fe³⁺ in solution and this metallic specie precipitates into the soil phase, as can be seen in Fig. 2. Based on these results, ferrous iron was chosen to impregnate soil before adding H₂O₂ in the Fenton's reaction. Fe(II) serves as catalysts in the Fenton's reactions, where HO[•] is generated by direct reaction of H₂O₂ and Fe(II).

To quantify the precipitation of dissolved iron on the surface a mass balance on Fe(II) in the liquid phase according to the Eq. (2).

$$q = \frac{(C_0 - C_f)V_L}{W} \quad (2)$$

where q is the iron content in soil (mg g⁻¹), C_0 and C_f are the initial and final soluble iron concentration in the liquid phase, V_L is the volume of the iron sulphate solution (mL) and W is the weight soil sample (g). Due to precipitation, the soil containing iron(II) was

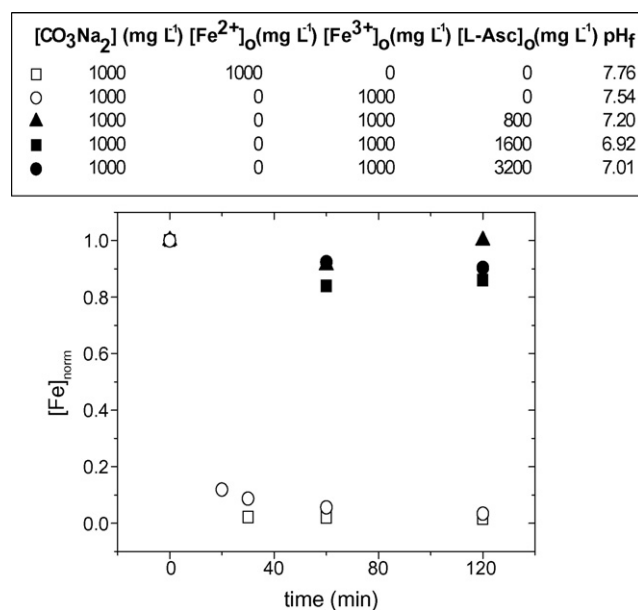


Fig. 1. Soluble iron content in aqueous media.

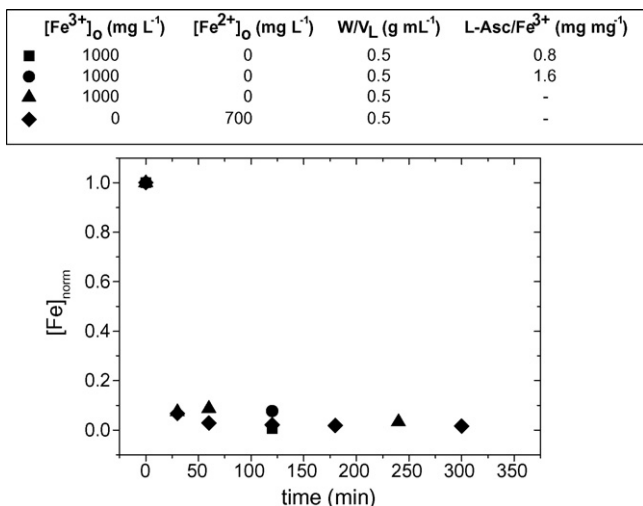


Fig. 2. Soluble iron content in water-soil slurries.

used in the heterogeneous catalyzed H₂O₂ system. The ferrous iron content in the soil achieved for the hydrogen peroxide decomposition and 2,4-DMP degradation experiments was 2.1 mg_{Fe} g⁻¹.

3.2. Adsorption 2,4-DMP isotherm

The adsorption equilibrium data of 2,4-DMP is shown in Fig. 3, where q (mg g⁻¹) is the adsorbed phase concentration, and C_{eq} (mg L⁻¹) is the liquid phase concentration. Sorption of the organic compound was calculated from the difference between initial and final concentration.

It is well known that the binding capacity of an organic compound to the soil is generally a direct function of the soil organic content. Moreover, if the polarity of the pollutants increases, the soil adsorption capacity decreases [16]. In the case of 2,4-DMP this pollutant is strongly sorbed to soil as expected from its hydrophobicity and the high OM content of the soil employed.

3.3. Hydrogen peroxide decomposition

The three variables investigated for hydrogen peroxide decomposition in soil samples were H₂O₂ concentration (1000–25,000 mg L⁻¹), slurry density (0.25–1 g_{soil} mL⁻¹) and iron(II) amount in the soil (2.1 mg_{Fe} g⁻¹). Batch experiments were conducted in order to provide conclusive evidence whether the iron

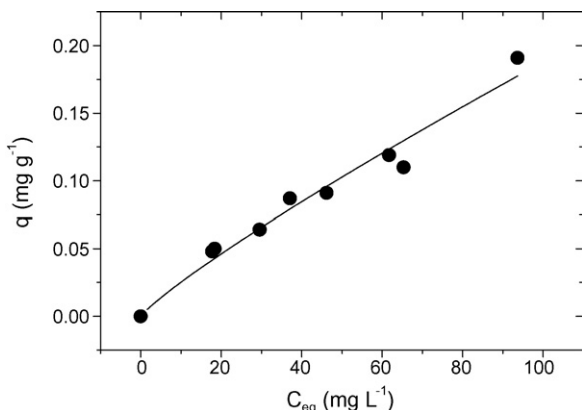


Fig. 3. Adsorption isotherm of 2,4-DMP.

content or the organic content of the soil was the responsible for the decomposition of hydrogen peroxide.

The hydrogen peroxide decomposition data vs. time, without the addition of iron sulphate, are reported in Fig. 4, for two different initial hydrogen peroxide concentrations, equal to 10,000 and 17,000 mg L⁻¹. The concentration of hydrogen peroxide progressively decreased as a function of the time. The data show that the hydrogen peroxide decomposition rate increased with the concentration of soil in the system. The natural organic matter of the soil was expected to be responsible for the consumption of hydrogen peroxide. If the decomposition of the hydrogen peroxide presents a heterogeneous way the following proportionality could be obtained:

$$\frac{-d[\text{H}_2\text{O}_2]}{dt} \propto \frac{W}{V_L} \quad (3)$$

The heterogeneous decomposition of the H₂O₂ by the soil is proved with data in Fig. 5a where the normalized hydrogen peroxide profile is plotted against the product $t \cdot W/V_L$ and a sole curve is obtained.

The results obtained for the H₂O₂ decomposition if the iron is previously precipitated are shown in Fig. 5b. It can be seen that the previous addition of iron sulphate to the soil decreased the hydrogen peroxide decomposition.

3.4. 2,4-DMP in situ oxidation

A soil polluted with 2,4-DMP was used to impregnate the ferrous iron of the ferrous sulphate solution. After centrifugation of the supernatant and drying the soil, the content in 2,4-DMP and Fe(II) was calculated from a mass balance obtaining $q_{2,4\text{-DMP}} = 0.11 \text{ mg g}_{\text{soil}}^{-1}$ and $q_{\text{Fe}} = 2.1 \text{ mg g}_{\text{soil}}^{-1}$. This polluted soil containing the catalytic specie was used in the modified Fenton's runs. The runs were carried out as described in the Method section. The H₂O₂ was added in excess (10,000 and 20,000 mg L⁻¹). The need for excess H₂O₂ results from its non-specific losses due to decomposition in the presence of reactive materials in soils in addition to the reaction with 2,4-DMP. The theoretical H₂O₂ demand for the total mineralization of the sorbed 2,4-DMP has been calculated as 307 mg L⁻¹ in the experimental conditions.

The supernatant was separated by centrifugation after 20 minutes of reaction time, and ecotoxicity, 2,4-DMP, organic acids produced and solubilized iron were measured by Microtox[®], GC, IC and ICP-AES, respectively, at the conditions described above. Results are shown in Table 3. The samples were not toxic and the 2,4-DMP was not detected in water phase after Fenton treatment in all experiments. Moreover, the iron content in this supernatant was found a negligible amount.

The potential toxic intermediates of the 2,4-DMP oxidation were determined by Microtox[®] after sonication and centrifugation, as described in the experimental section. The Toxicity units obtained (<2) were lower than the expected from the initial 2,4-DMP sorbed ($q = 0.11 \text{ mg g}^{-1}$). This expected value would be about TUs = 7 having into account the EC₅₀ of the 2,4-DMP (3.55 mg L⁻¹) [24] and the ratio W/V_L used in the sonication (1 g_{soil}/5 mL of Milli-Q water). Therefore, it can be concluded that no toxic intermediates are produced in the remediation of the soil polluted with 2,4-DMP by using this heterogeneous Fenton treatment.

The residual pollutant in the soil was measured by extraction with methanol in an ultrasonic bath as it was described in the previous section. The efficiency of this last extraction was tested using blank samples polluted with a known amount of the 2,4-DMP. After four extraction steps, pollutant in the methanolic phase obtained after extraction of the blank samples was near to 90% of the initial pollutant in the soil. With this extraction efficiency the value of the

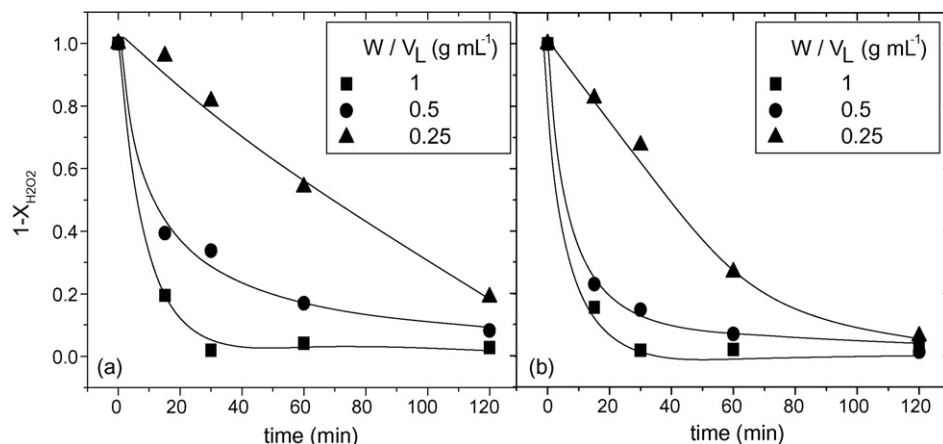


Fig. 4. Decomposition of H_2O_2 at different initial concentrations and W/V_L ratios. (a) $[\text{H}_2\text{O}_2]_0 = 10,000 \text{ mg L}^{-1}$. (b) $[\text{H}_2\text{O}_2]_0 = 17,000 \text{ mg L}^{-1}$.

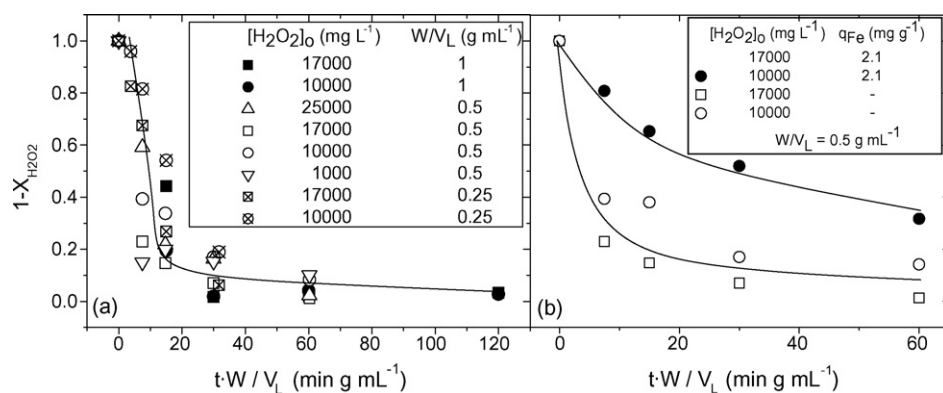


Fig. 5. Decomposition of H_2O_2 in batch system in the presence and absence of $\text{Fe}(\text{II})$.

Table 2

Operating conditions of contaminant degradation batch tests

RUN	$[\text{H}_2\text{O}_2]_0$ (mg L^{-1})	W_{soil} (g)	W/V_L (g mL^{-1})	q_{Fe} (mg g^{-1})	$q_{2,4\text{-DMP}}$ (mg g^{-1})	2,4-DMP (mg C)	Reaction time (min)
1	10,000	1	0.5	2.1	11×10^{-2}	8.7×10^{-2}	20
2	20,000	1	0.5	2.1	11×10^{-2}	8.7×10^{-2}	20

2,4-DMP residual amount in the soil can be calculated. The results of 2,4-DMP oxidation experiments are reported in Table 3. As it can be seen, the 2,4-DMP removal increases with higher concentrations of H_2O_2 .

On the other hand, the only acid detected from the 2,4-DMP oxidation was acetic acid, being found in the supernatant obtained after centrifugation. To relate both compounds, the pollutant and the acetic acid have been expressed as mg of carbon. These values are also summarized in Tables 2 and 3. The appearance of significant amounts of this acid proves that the oxidation of the pollutant is taken place and no toxic intermediates are release to the aqueous phase. No acetic acid appears when soil free of pollutant is treated by Fenton's reagent.

Table 3

Summarized results for Fenton's destruction of 2,4-DMP in soil slurries

RUN	2,4-DMP supernatant (mg C)	2,4-DMP soil (mg C)	$X_{2,4\text{-DMP}}$ (%)	Acetic acid supernatant (mg C)
1	0	2.2×10^{-2}	75	2×10^{-2}
2	0	1.2×10^{-2}	86	7×10^{-2}

Mechanisms of various organic contaminants susceptible to Fenton's reaction have been documented [25]. Fenton's chemistry is a complex collection of reaction pathways as can be seen in the Table 4 [8]. A mechanism which includes heterogeneous and homogeneous free-radical reactions was developed to describe the chemical interpretation of the obtained results. When sufficient quantities of $\cdot\text{OH}$ are generated, Fenton's reagent is a potential method for rapidly destroying contaminants primarily in the aqueous phase.

It has been proposed that $\cdot\text{OH}$ can also directly attack contaminants sorbed on soils (Reactions 19 and 20 in Table 4). Fenton-like catalysis (heterogeneous Fenton's reactions) utilizing H_2O_2 and iron minerals have the potential to oxidize sorbed contaminants has been examined in some studies [26]. The development of active heterogeneous Fenton systems, where soluble Fe^{+2} is replaced by Fe-containing solids with no need of low pH is of considerable interest. In this study, at neutral pH, dissolved iron cation is lost by precipitation. In addition, in the presence of natural organic matter (NOM) in soil, dissolved iron cation may be lost via binding with hydrophilic sites (e.g., $-\text{OH}$, $-\text{COOH}$) of NOM. This modified Fenton system has been designed particularly to remediate 2,4-DMP sorbed at pH-neutral soil.

Table 4
Proposed reactions for contaminant destruction by heterogeneous Fenton's reactions in soil slurries [8]

	No.
Principle Fenton radical reactions in the aqueous phase	
$\bullet\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{O}_2^{\bullet-} + \text{H}_2\text{O}$	(1)
$2\bullet\text{OH} \rightarrow \text{H}_2\text{O}_2$	(2)
$\text{HO}_2^{\bullet} \leftrightarrow \text{O}_2^{\bullet-} + \text{H}^+$	(3)
$\text{HO}_2^{\bullet} + \text{O}_2^{\bullet-} \rightarrow \text{HO}_2^- + \text{O}_2$	(4)
$\bullet\text{OH} + \text{HO}_2^{\bullet} \rightarrow \text{H}_2\text{O} + \text{O}_2$	(5)
$\bullet\text{OH} + \text{O}_2^{\bullet-} \rightarrow \text{OH}^- + \text{O}_2$	(6)
Reactions associated with carbonate species	
$\text{CO}_{2(\text{g})} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_{3(\text{aq})}$	(7)
$\text{H}_2\text{CO}_{3(\text{aq})} \leftrightarrow \text{HCO}_3^- + \text{H}^+$	(8)
$\text{HCO}_3^- + \bullet\text{OH} \rightarrow \text{CO}_3^{\bullet-} + \text{OH}^-$	(9)
$\text{CO}_3^{\bullet-} + \text{H}_2\text{O}_2^{\bullet} \rightarrow \text{HO}_2 + \text{HCO}_3^-$	(10)
$2\text{CO}_3^{\bullet-} \rightarrow \text{products}$	(11)
$\text{CaCO}_{3(\text{s})} + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$	(12)
Reaction associated with natural organic matter (NOM)	
$\text{NOM} + \bullet\text{OH} \rightarrow \text{products}$	(13)
Soil mineral surface catalysed reactions and reactions associated with sorbed contaminant (R)	
$\text{Fe}_{\text{red}(\text{s})} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}_{\text{ox}(\text{s})} + \bullet\text{OH}$	(14)
$\text{Fe}_{\text{ox}(\text{s})} + \text{H}_2\text{PO}_2 \rightarrow \text{Fe}_{\text{red}(\text{s})} + \text{HO}_2^{\bullet}$	(15)
$\text{Fe}_{\text{red}(\text{s})} + \bullet\text{OH} \rightarrow \text{Fe}_{\text{ox}(\text{s})} + \text{OH}^-$	(16)
$\text{Fe}_{\text{red}(\text{s})} + \text{HO}_2^{\bullet} \rightarrow \text{Fe}_{\text{ox}(\text{s})} + \text{H}_2\text{O}_2$	(17)
$\text{Fe}_{\text{ox}(\text{s})} + \text{O}_2^{\bullet-} \rightarrow \text{Fe}_{\text{red}(\text{s})} + \text{O}_2$	(18)
$\bullet\text{OH} + \text{R}_{(\text{ads})} \rightarrow \bullet\text{ROH}_{(\text{ads})}$	(19)
$\bullet\text{ROH}_{(\text{ads})} + \text{Fe}_{\text{ox}(\text{s})} \rightarrow \text{Fe}_{\text{red}(\text{s})} + \text{ROH}_{(\text{ads})}$	(20)

$\text{Fe}_{\text{red}(\text{s})}$ and $\text{Fe}_{\text{ox}(\text{s})}$ are reduced and oxidized iron oxyhydroxide surface sites.

4. Conclusions

The Fenton-like process using a soil impregnated with iron and further addition of hydrogen peroxide has been proved to be effective in the abatement of strongly sorbed pollutants, as 2,4-DMP. This procedure allows the use of pH-neutral and even higher pH conditions thus avoiding the acidification of the soil that could produce a strongly negative environmental impact. An excess of H_2O_2 is necessary while this reactant is heterogeneously decomposed by the soil. An additional advantage of the previous precipitation-impregnation of Fe(II) into the soil is that the decomposition of the hydrogen peroxide is significantly slower in presence of this sorbed/precipitated iron.

The reaction can be supposed is taking place at the soil surface because the catalytic specie (Fe) is not leached to the aqueous phase of the slurry system.

The more toxic intermediate from the 2,4-DMP oxidation using Fenton reagent in an homogeneous way is 2,4 dimethylcatechol. This compound was not detected in the soil remediation applied here. Moreover, with the ecotoxicity measurements we can conclude that no toxic intermediates are produced in the heterogeneous Fenton runs.

Acknowledgements

The authors acknowledge financial support for this research from the Spanish MEC provided throughout projects CTQ2004-07019 and CTM2006-00317.

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