

Abiotic oxidation of catechol by soil metal oxides

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Abstract

The mechanism of catechol oxidation by soil metal oxides is investigated in a slurry reactor. This abiotic transformation is shown to consist in a three-step process.

The first step is a heterogeneous reaction. Catechol undergoes fast, partial oxidation at the expenses of Fe and Mn oxides contained in the soil. In the second step, reduced Fe and Mn are released into the aqueous solution and immediately complexed by catechol. Metal-catecholate complexes are stable at the very low dissolved-oxygen concentration levels attained under nitrogen sparging.

The third step is a homogenous reaction. The highly reactive intermediate produced by catechol partial oxidation initiates catechol polymerisation. Under nitrogen sparging, the polymerisation process ends rather rapidly, thus yielding only partial conversion of the phenol and producing low-molecular weight, water-soluble polymers. Further oxidation of the metal-catecholate complexes formed in the second step only occurs under air sparging. Thus, reactive intermediates are formed at much higher concentration levels than those attained when nearly no oxygen is present in solution. The polymerisation proceeds at a much faster rate until, under the experimental conditions adopted, complete catechol conversion is attained and high-molecular-weight, insoluble polymers are produced.

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1. Introduction

The treatment of phenolics in water solution within an aerated soil slurry was analysed by Colarieti et al. [1]. The observed, marked reduction in phenolic content was attributed to polymerisation brought about by clay minerals and was entirely abiotic in nature, since it was unaffected by soil sterilisation. In soil-activity tests with different phenolic compounds, *o*-diphenols had the highest reactivity. The rate of catechol (*o*-dihydroxybenzene) removal was first-order with respect to both catechol and soil concentration.

The process is of relevant environmental interest for soil remediation, since catechol is a key intermediate in the microbial degradation of aromatic compounds [2]. Furthermore, catechol is highly representative of the *o*-diphenols released in actual phe-

nolic wastewaters, such as those produced in olive mills. Because of the lack of economically compatible treatments, spreading of Olive Mill Wastewater (OMW) onto agricultural soils is a fairly common practice in most olive oil producing countries. In the long period, the antimicrobial and phytotoxic activity of polyphenols negatively affects soil fertility. This situation is crucial and widespread in all the Mediterranean basin, where more than 90% of the world production of olive oil is localised. This further increases the interest for a deeper analysis of the interactions between phenolic aqueous solutions and soil components, even though soil is a complex and not precisely defined system.

The oxidation of phenolic compounds by metal oxides is well documented in the literature, both in soil and in model systems [3–11]. It is widely accepted that phenol oxidation takes place according to the following two-step mechanism: phenols interact onto the metal (Fe, Mn) oxide surface and cause metal reduction while undergoing a simultaneous oxidation to the corresponding semiquinone or quinone. Both semiquinone and quinone start phenol polymerisation giving rise to insoluble, humus-like polymers. In the presence of dissolved oxygen and/or of high metal-oxide to phenol ratios, more drastic oxidation takes

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place resulting in ring fission and even in CO₂ production, as reported by Naidja et al. [12] and Wang and Huang [13]. At alkaline pH and in the presence of dissolved oxygen, solubilised Fe and Mn are re-oxidised, thus restoring the initial oxidation state.

Basic purpose of this paper is to elucidate further the mechanism of abiotic transformation of catechol by the complex soil-system.

2. Materials and methods

2.1. Soil samples

The unpolluted soil used in most experimental runs was sampled from a loess layer at 3.2–3.5 m depth in an industrial site at Rositz, near the city of Altenburg (East-Thuringia, Germany) and has been characterised in a previous investigation [1]. Its relevant characteristics are reported in Table 1.

Further tests were carried out on three more soil samples, all of them corresponding to agricultural soils, representative of different situations within the Mediterranean basin. Their relevant characteristics are reported in Table 1.

Physico-chemical characterization was carried out on air-dried samples sieved at 2 mm. Texture determination was carried out by the pipette method [14]. Soil pH was measured in 3:10 soil/water suspension. Organic matter content was determined by dichromate oxidation [15]. Total amounts of Mn and Fe were measured by atomic absorption spectroscopy (AAS) after soil digestion with a hot nitric-chloridric solution [16]. On the Rositz soil sample, extraction of Fe and Mn was also performed by the citrate-bicarbonate-dithionite (CBD) method [17]. Correspondingly, lower amounts of Fe (0.120 mmol/g dry soil) and Mn (0.005 mmol/g dry soil) were then measured by AAS. This is reasonable since the CBD method only accounts for the contribution of fine-grained, amorphous Fe and Mn oxides. According to Lehmann et al. [4], only CBD-extractable Fe and Mn oxides are involved in the redox reaction with phenolic acids.

2.2. Slurry reactors

All reaction experiments were carried out at 20 °C in stirred slurry reactors, as described in [1], under continuous gas sparging (either nitrogen or air).

The reactor consisted in a Pyrex-glass vessel (overall volume 220 mL), equipped with a two-blade impeller driven by a small electric motor (220 rpm). Ports were present for suspension sampling and for continuous gas sparging and venting. Gas

flow-rates were measured by a bubble flow-rate meter. Under the experimental conditions adopted, the rate of oxygen gas-liquid mass-transfer was sufficient to ensure near-equilibrium values for dissolved oxygen concentration even in the presence of oxygen-consuming reactions (see [1] for details).

The reaction was started by adding catechol to a suspension of 240 g of dry soil per litre of distilled water to yield a final catechol concentration of 5.26 mmol/L. The amounts of soil were the same for all soils.

Reference runs were performed with manganese oxide (Mn(IV) oxide, “activated”, from Sigma-Aldrich). Extractable manganese content determined by CBD method was 11.5 mmol/g. In these experiments, 0.21 g of manganese oxide were added per litre of distilled water, to yield a final, overall Mn concentration roughly equivalent to that of the reference (Rositz) soil sample.

Water suspensions of the reference soil had an intrinsic pH value of 8 ± 0.3 that remained virtually unchanged in the course of the experimental runs, both in the presence and in the absence of catechol, both with oxygen and with nitrogen sparging. Therefore, no addition of acid or base or buffer solutions was required to keep the pH constant. pH values of approximately 8, that remained constant throughout, were achieved with the other soil samples and with manganese oxide, as well.

In the experimental runs under nitrogen sparging, the slurry and the concentrated catechol solution were kept separately under nitrogen bubbling for 30 min. The run was started by rapidly mixing the catechol solution and the slurry. The reactor was continuously kept under gas sparging (either nitrogen or air).

Direct dissolved-oxygen measurements performed in the reactor in the absence of soil, i.e. in distilled water, after 30 min of nitrogen sparging, indicate a residual oxygen concentration of 0.03 ± 0.01 mmol/L (by iodometry [18]). Thus, in spite of nitrogen sparging, the system is not entirely oxygen-free.

About 2 mL-samples of slurry were drawn periodically. The samples were centrifuged at $1400 \times g$ for 5 min. The supernatant was then filtered with a 0.2 µm filter (cellulose acetate, Sartorius, Göttingen, Germany).

The following determinations were carried out:

- Residual catechol concentration, by reversed-phase HPLC (Shimadzu, equipped with a C-18 column from Waters-Spherisorb, eluent 70:30 acidified water:acetonitrile, detection at 280 nm); average measurement error is $\pm 1.2\%$ (95% confidence based on up to five measurements).
- Fe and Mn concentration, by AAS (atomic absorption spectrometry, AAnalyst 100 Perkin-Elmer); average measurement

Table 1
Physico-chemical characteristics of soil samples from different sources

Site	pH	Sand (%)	Silt (%)	Clay (%)	Organic matter (%)	Total Fe (mmol/g)	Total Mn (mmol/g)
Castelvoturno (Naples, Italy)	8.2	20.1	32.2	47.7	4.70	0.50	0.030
Marrakech (Morocco)	8.4	47.3	23.0	29.7	2.16	0.50	0.010
Rositz (Thüringen, Germany)	8.0	4.20	73.60	21.50	0.40	0.39	0.010
Chaal (Sfax, Tunisia)	8.1	89.00	1.50	8.52	0.16	0.10	0.003

error is less than $\pm 5\%$ (95% confidence based on three measurements).

- TOC (total organic carbon content) by the catalytic oxidation method (Shimadzu 5000A TOC Analyzer); average measurement error is $\pm 4.3\%$ (95% confidence based on up to five measurements).
- Absorption spectrum in the range 360–800 nm, on a Shimadzu UV-1601 spectrophotometer.

3. Results and discussion

3.1. Catechol conversion under nitrogen sparging

Catechol concentration in the reference soil slurry (Rositz) under nitrogen sparging is shown in Fig. 1, as a function of reaction time. Catechol concentration suddenly decreases from 5.26 to 3.90 mmol/L. The first experimental measurement was performed after 3 min from soil addition. Subsequently, a non-zero, steady-state concentration is attained in approximately 3 h. The solution develops a marked blue-color.

Along with catechol disappearance, iron and manganese are released into the solution, as shown in Figs. 2 and 3.

It should be noted that, in the absence of catechol, i.e. in soil suspensions in distilled water, the concentration of both iron and manganese is negligible. On the contrary, in catechol solutions, after an initial, sudden release, iron concentration further increases in the following 3 h, until a seemingly asymptotic value is reached. In the same time interval, catechol concentration reaches an asymptote, as well. The same, sudden release occurs for manganese. After a very fast and limited drop from the initial value, manganese concentration remains approximately constant throughout, though at much lower levels, as compared to iron.

The measured TOC of samples collected at 3 min is 370 ± 6 mg/L. This exceeds that pertaining to the corresponding,

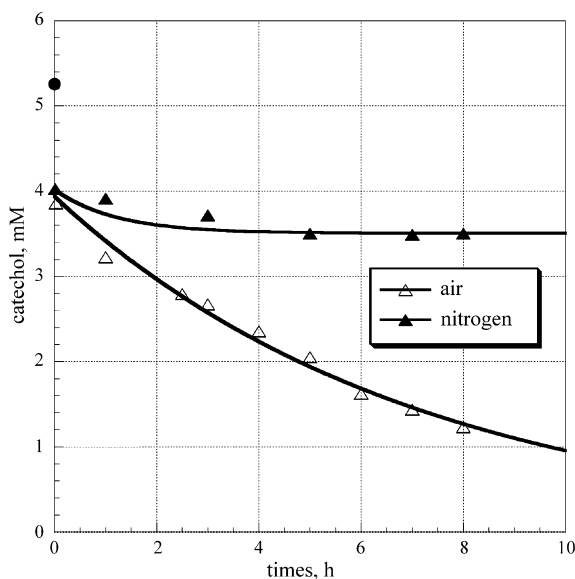


Fig. 1. Soil slurry with catechol under nitrogen or air sparging: time course of catechol removal.

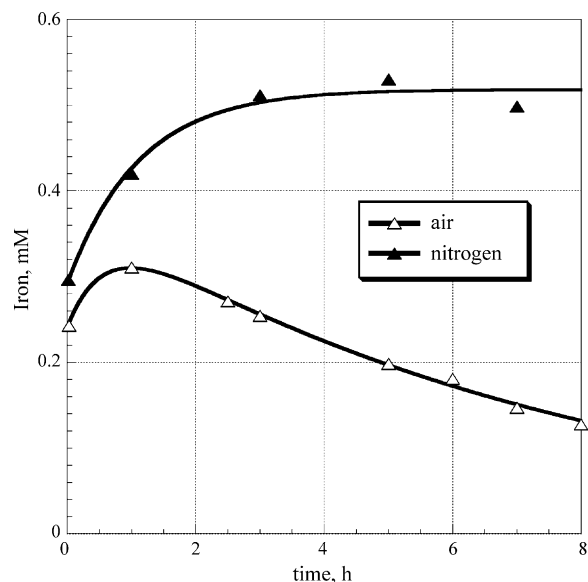


Fig. 2. Soil slurry with catechol under nitrogen or air sparging: time course of Fe release from the soil.

measured catechol concentration (4.0 mmol/L, yielding a theoretical TOC of 290 mg/L), while coinciding with that (379 mg/L) pertaining to the initial catechol concentration (5.26 mmol/L). The contribution to TOC due to the organic matter released by soil is negligible, as shown by separate measurements on soil suspensions in distilled water. Therefore, the removal of catechol observed after 3 min is not due to adsorption onto the soil matrix, to mineralization, to the formation of polymeric aggregates of such dimension as to be captured by a $0.2 \mu\text{m}$ membrane. Indeed, all these mechanisms would necessarily result in a reduction in the TOC of the filtered supernatant, as compared to the initial value of 379 mg/L. This result clearly suggests that catechol is converted into soluble compounds that still contribute to the TOC reading.

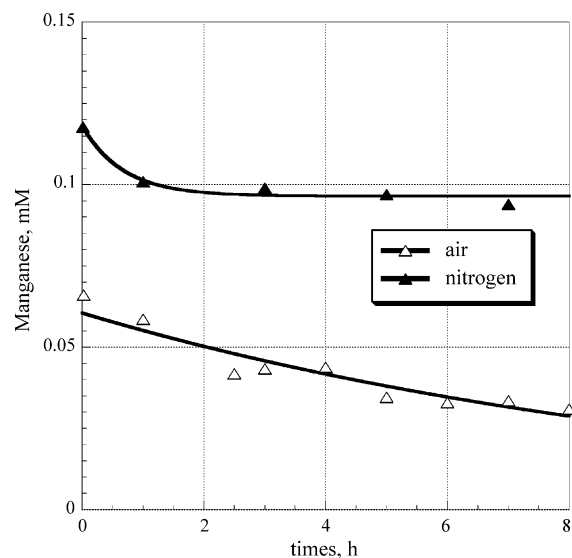


Fig. 3. Soil slurry with catechol under nitrogen or air sparging: time course of Mn release from the soil.

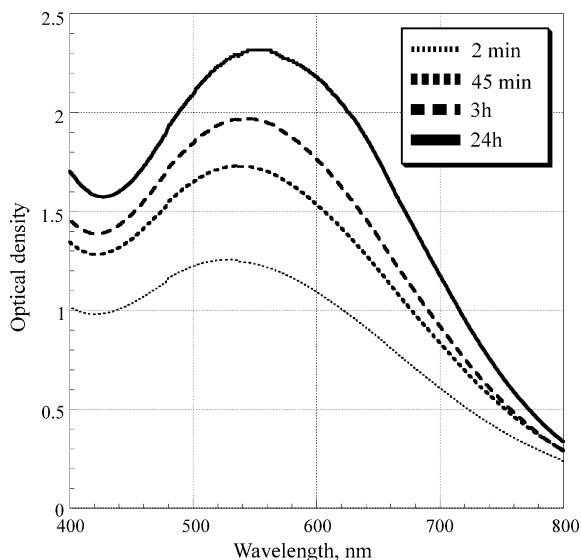


Fig. 4. Soil slurry with catechol under nitrogen: absorbance spectra of supernatant samples taken at different times.

The form under which metals are present in the supernatant needs elucidation. It is well known that catechol has a strong metal-complexing ability towards iron. At alkaline pH, mono- and bis-complexes are formed with Fe(II) [19–21], whereas bis- and tris-catecholate complexes are formed with Fe(III) [20,22].

Absorbance spectra of supernatant samples from a run performed under nitrogen sparging are reported in Fig. 4. It can be seen that a broad absorption band appears at approximately 500–550 nm, whereas the spectra pertaining to pure catechol in aqueous solution show the characteristic aromatic band at 280 nm and no absorption at all in the visible range. The maximum absorbance increases continuously in the course of time, closely following iron concentration in the supernatant (Fig. 2).

The absorption spectra closely resemble that pertaining to Fe(III)-catecholate, as obtained by Avdeef et al. [22] and Kipton et al. [20]. In order to further accrue the hypothesis that Fe(III)-catecholate complexes are actually formed in the course of our experimental runs, tests were performed by varying the pH by addition of concentrated HCl or NaOH under constant nitrogen sparging. Rearrangements in spectra ensuing pH changes are instantaneous and iron concentration, as measured by AAS, is unaffected. In Fig. 5, the wavelength λ_{\max} at which the maximum absorption is attained in supernatant spectra is reported as a function of pH. The data closely match those obtained by Avdeef et al. [22] and Kipton et al. [20] with model solutions of Fe(III)-catecholate. This clearly indicates that Fe(III)-catecholate complexes are formed in our experimental runs, as well.

The absorbance at 505 nm of supernatant samples drawn from the slurry reactor at different reaction times is used to estimate the corresponding concentration of iron-catechol complexes, by using the extinction coefficient ϵ_{505} of $3.30 \pm 0.10 \text{ L (mmol cm)}^{-1}$, as determined directly on model solutions of catechol and FeCl₃ prepared at pH 8. The estimated concentrations of Fe(III)-catecholate complexes at 3 min and 3 h are 0.34 and 0.56 mmol/L, respectively. These values are in good agreement with the overall iron concentration, as determined by

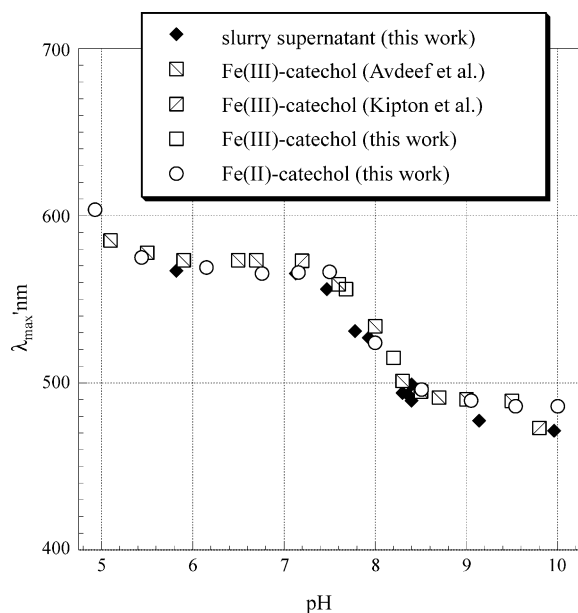


Fig. 5. Dependence of wavelength of light absorption maximum on pH for supernatant samples and for Fe(II)- and Fe(III)-catecholate solutions, Fe(III)-catecholate data from Avdeef et al. [19] and Kipton et al. [17].

AAS (0.30 and 0.51 mmol/L, respectively). Thus, all iron in solution is under the form of Fe(III)-catecholate complexes.

On the basis of the reaction scheme generally accepted in the Literature and summarized in Section 1, catechol oxidation takes place with the simultaneous reduction of soil metal oxides to soluble Fe(II) and Mn(II). Therefore, as regards iron, one would expect Fe(II)-catecholate complexes to be formed instead of Fe(III)-catecholate.

Further absorption spectra were measured on model systems under exactly the same experimental conditions as the slurry experiments, in terms of pH, temperature and continuous nitrogen sparging with the same catechol and iron concentration (5.26 and 0.54 mmol/L, respectively). The only difference is that iron was present as FeCl₂. The resulting pH-dependence of the maximum absorption wavelength is reported in Fig. 5. It can be seen that it superimposes with those obtained in the course of our standard experiments and with those by Avdeef et al. [22] and Kipton et al. [20], as well.

Again, the conclusion must be reached that Fe(III)-catecholate complexes are formed in the model system. As already outlined in Section 2, this confirms that, in spite of nitrogen sparging, our experimental system is not sufficiently oxygen-free, as to prevent the spontaneous oxidation of Fe(II) to Fe(III).

The slurry reactor experiments indicate that, upon interaction between soil and catechol, manganese is released into the supernatant, as well. The Literature reports that catechol forms complexes with manganese. Mn(II)-catecholate complexes are reported by Tyson and Martell [19] and by Dubey and Nepal [21]. Mn(III)-tris-catecholate complexes are produced at alkaline pH according to Magers et al. [23]. These manganese complexes have a broad absorbance band between 550 and 750 nm. The corresponding extinction coefficients are much lower than those

pertaining to iron-catechol complexes (cf. [22,23]). Therefore, in our absorbance spectra with soil, the absorbance of manganese complexes, if present, is masked by that of iron complexes.

3.2. Catechol conversion under air sparging

Catechol removal in a soil slurry (Rositz sample) under air sparging is shown as a function of reaction time in Fig. 1. After 3 min from soil addition, catechol concentration drops from 5.26 to 3.90 mmol/L, i.e. to the same value observed in the run under nitrogen sparging. After this initial, fast decay, however, catechol concentration undergoes a further, continuous decrease until complete conversion is attained (usually in 24 h, under the experimental conditions adopted, data not shown). The decay follows an exponential curve, indicative of first-order kinetics with respect to catechol concentration. Reference tests show that catechol autoxidation by dissolved molecular oxygen at pH 8 is negligible in the time span of experiments. Therefore, the observed conversion is entirely due to reactions promoted by soil.

A time-progressive blackening of the solution is observed, as well. This can be attributed to the formation of insoluble polymers, since black material is recovered by sample filtration. Furthermore, the TOC of filtered supernatant samples continuously decreases, in parallel with polymer formation, in the time course of the experiment (see also [1]). Residual TOC after 24 h (total conversion of catechol) is 102 ± 3 mg/mL.

Since the amounts of CO_2 measured in the effluent gas from the reactor (data not shown), were negligible, mineralization is ruled out as a possible cause for the observed TOC decay. Indeed, CO_2 production is reported to take place in the presence of much higher metal oxide/catechol ratios than those used in this work [12,13]. Furthermore, the long time-scale of catechol removal is hardly compatible with the short one typical of adsorption.

Again, along with catechol disappearance, iron and manganese are released into the solution, as shown in Figs. 2 and 3, respectively. After 3 min, the concentration of both iron and manganese suddenly increases from the zero value pertaining to soil suspensions in distilled water to 0.24 and 0.07 mmol/L, respectively. These are close to the concentration levels attained at the same reaction time under nitrogen sparging. After this initial outburst, iron concentration achieves its maximum within 1 h, approximately. Then, a continuous, exponential decrease takes place. As regards soluble manganese, after the initial release, an exponential decrease is observed, as well.

Under air sparging, an absorbance band is apparent in the same wavelength region as that observed under nitrogen sparging (Fig. 6). Again, this suggests that Fe(III)-catecholate complexes are formed. The absorbance values increase with time, achieving a maximum in approximately 1 h, and then decay. This mirrors the behaviour of iron concentration. Fe(III) complexes seem to accumulate in the first phase of the reaction and then to decrease, along with residual catechol.

The time course of catechol conversion and metal solubilization suggests a three-step process. Within 3 min from soil addition, catechol disappearance is due to the same redox reactions involving catechol and metal oxides observed under nitrogen

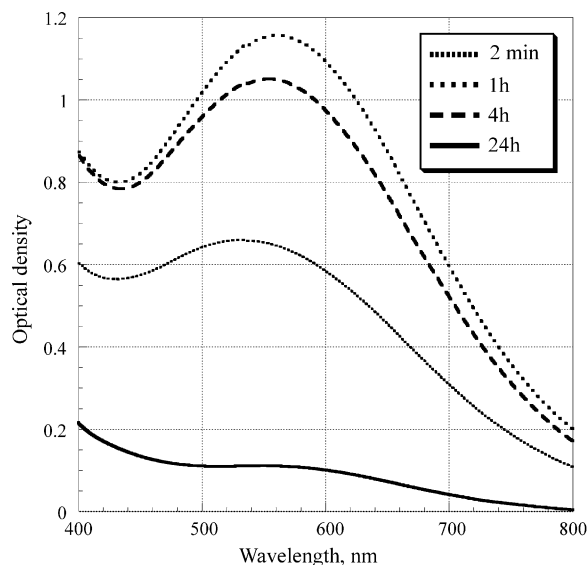


Fig. 6. Soil slurry with catechol under air sparging: absorbance spectra of supernatant samples taken at different times.

sparging. The concurrent release of metals into the supernatant is due to the formation of complexes between catechol and reduced metals. The third, slower step yielding further catechol conversion and metal removal is due to a reaction involving dissolved, molecular oxygen. Obviously, under air sparging, dissolved oxygen achieves much higher concentration levels than the marginal ones present under nitrogen sparging.

Two further tests were carried out on the supernatant after soil removal, in order to verify whether or not the third oxidation step still involves soil oxides (Fig. 7).

At the beginning, the first run was performed under nitrogen sparging. Once the fast decrease in catechol concentration had

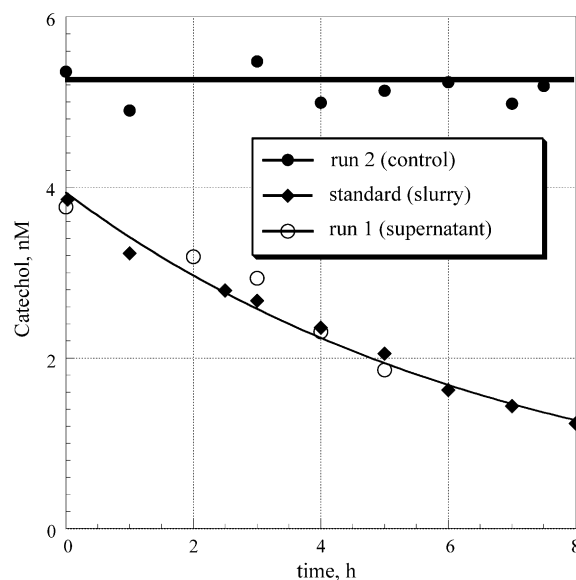


Fig. 7. Comparison of catechol removal course: in a soil slurry; in a solution obtained from a slurry with catechol after soil removal (run 1); in a control run with the solution obtained from a slurry with catechol added after soil removal (run 2).

occurred and most of iron and manganese had been released under the form of metal-catecholate complexes (see Figs. 1–3), i.e. after 1 h of contact-time between soil and catechol, the reactor content was centrifuged and the supernatant was recovered and filtered. A new reactor was filled with the supernatant and kept under air sparging. Catechol concentration was monitored as a function of time, as usual. The results are shown in Fig. 7, in direct comparison with those of Fig. 1. Although in the complete absence of soil, catechol conversion follows the same time course. The same time-progressive blackening of the solution was observed, as well.

A further run (run 2) was performed to test if the solubilization of an unrecognized catalyst from the soil matrix occurred, independently of catechol addition. Initially, no catechol was added and the soil suspension in distilled water was kept under nitrogen sparging for 1 h. The reactor content was centrifuged. The supernatant was filtered and catechol was added to reach the initial concentration of 5.26 mmol/L. A new reactor was filled, air started being sparged, and catechol concentration was monitored for 8 h. No catechol conversion was measured (Fig. 7). Therefore, catechol and soil must be present simultaneously in order to produce the reactive species.

Metal-catalyzed oxidation of catechol by molecular oxygen in aqueous solution has been reported by several authors (see [24] for a review). For catechol oxidation in the presence of Fe(II) or Mn(II), both added as soluble salts, the reaction is described [25] as occurring through the formation of a metal-catecholate complex, followed by successive one-electron transfer to molecular oxygen from the metal ion. Intra-molecular electron transfers in the metal complex result in the formation of the quinone and regeneration of the lower oxidation state of metal ion. *O*-quinone is highly reactive and thus able to couple and to form polymers [26–28].

The oxidation of iron-catecholate complexes by molecular oxygen is supported by spectroscopic data in the Literature. Avdeef et al. [22] and Magers et al. [23] found that Fe(III)-catecholate complexes are stable in the absence of oxygen in mild alkaline solutions, whereas radical species (semiquinone) are detected by EPR in the presence of oxygen. The irreversible formation of uncharacterised products has also been reported.

The evidences gathered in the course of our experiments suggest that indeed oxygen does break the Fe(III)-catecholate complex, as shown by the time-progressive reduction of both the characteristic absorbance band and of the iron concentration, taking place in the supernatant after the initial outburst. The radical species thus produced promotes further catechol conversion through polymerisation. Therefore, at least one of the unidentified reactive species formed upon interaction between soil and catechol consists in iron-catecholate complexes, whose presence in the slurry reactor was detected directly by absorbance spectrophotometry.

On the basis of literature indications above cited, it is highly probable that the same mechanism is also followed by manganese, although the soil experiments provide no direct proof that Mn(III)-catecholate complexes are actually present in our slurry reactor. It should be noted, however, that, under nitrogen sparging, soluble manganese concentration in the super-

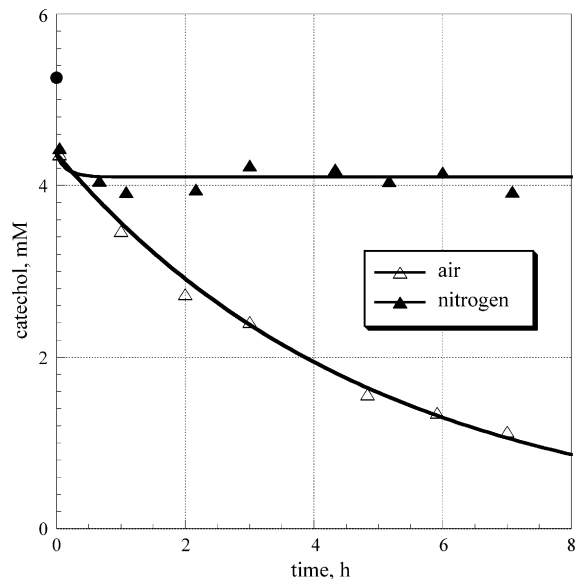


Fig. 8. MnO₂ slurry with catechol under nitrogen or air sparging: time course of catechol removal.

natant remains virtually constant, whereas, under air sparging, it decreases down to complete removal from the solution in 24 h (data not shown), thus closely following the same pattern as iron.

In order to point out the role of manganese, further experimental runs were carried out with a commercial manganese oxide, according to the procedures described in Section 2.2.

Upon interaction with catechol samples under nitrogen sparging, a broad absorption band in the visible range appears in the supernatant spectra, see Fig. 10, that matches that of Mn(III)-catecholate complexes reported in [23].

The amounts of manganese released both under nitrogen and air sparging (see Fig. 9) follow time-patterns closely resembling those of iron in soil experiments under the same experimental conditions (see Fig. 2).

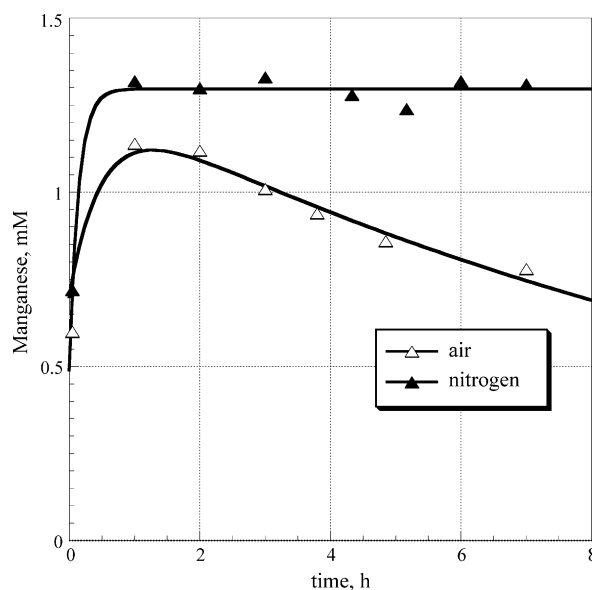


Fig. 9. MnO₂ slurry with catechol under nitrogen or air sparging: time course of Mn release.

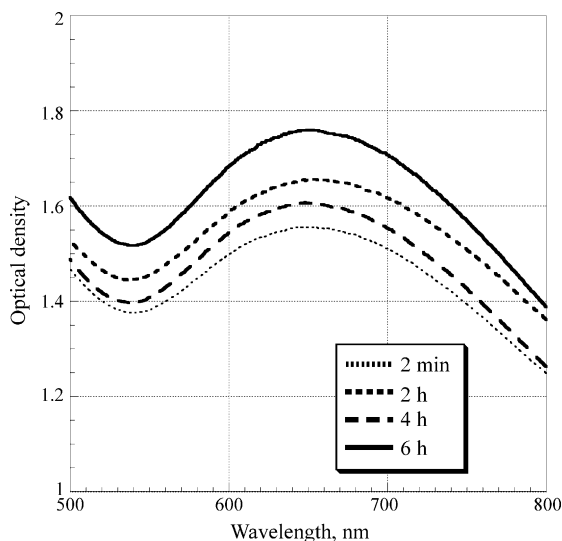


Fig. 10. MnO_2 slurry with catechol under nitrogen sparging: absorbance spectra of supernatant samples taken at different times.

On the basis of this experimental evidence, it seems fair enough to reach the conclusion that the same, three-step mechanism holds for both iron and manganese.

In the runs performed under nitrogen sparging and under air sparging, respectively, the amounts of catechol converted (see Fig. 8) follow time courses that strongly resemble those produced in soil experiments (see Fig. 1).

Even though the geographical origin of the soil is clearly immaterial, in view of an application to the treatment of OMW the use of a sample extracted from an industrial site in the heart of Eastern Germany seems rather peculiar, to put it mildly. The only reason for our first choice was that the Rositz soil samples we employed had been already well characterized in previous experiments.

We carried out further experimental tests with three different, undisturbed agricultural soils that are highly representative of the Mediterranean situation (see Section 2.1).

A complete set of experiments were performed on each soil, obtaining exactly the same general results as those discussed above, in terms of extremely fast metal release upon contact with catechol; catechol and metal decay with time; differences between corresponding runs under nitrogen and air sparging, respectively. Thus, the same, three-step reaction scheme applies even though the soil source and characteristics are widely different.

For the sake of comparison, only the data of catechol disappearance under air sparging are reported in Fig. 11, since these are the relevant results, in view of an application to OMW. The data are expressed as % residual catechol concentration with respect to the initial value achieved upon interaction between catechol and soil slurry.

The values of the initial, almost instantaneous decay in catechol concentration and of the first-order kinetic constant of catechol decay are both reported in Table 2 for each soil.

By cross-checking these data with those reported in Table 1, it is apparent that the higher the metal content of the soil sample,

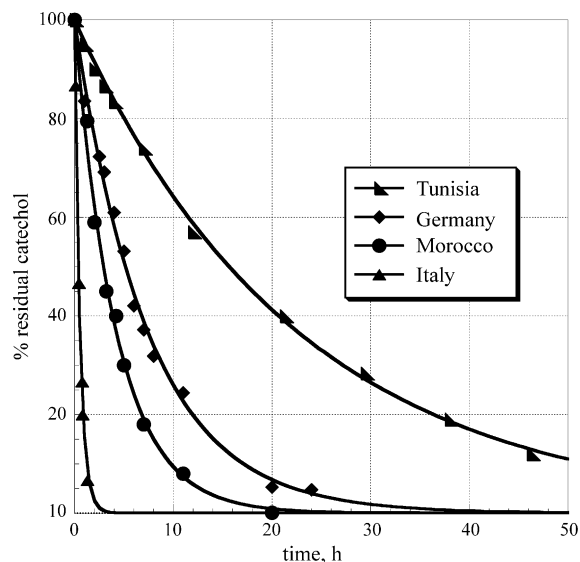


Fig. 11. Time course of catechol removal in soil slurries under air sparging. Comparison between different soil samples.

Table 2

Initial drop (after 3 min) and pseudo-first order kinetic constant for catechol removal in soil slurries

Soil sample	Initial catechol drop (mmol/L)	Kinetic constant (h^{-1})
Castelvoturno	3.2	1.830
Marrakech	1.8	0.236
Rositz	1.4	0.135
Chaal	0.0	0.044

the more marked is the effect of the treatment in terms of both instantaneous, initial drop in catechol concentration and rate of decay, as expected on the basis of the proposed reaction scheme.

4. Conclusions

A new, three-step reaction mechanism for catechol oxidation and polymerisation in a soil slurry is proposed. The three steps consist in: (i) metal oxides dissolution at the expenses of catechol; (ii) formation of complexes between reduced metal and residual catechol; (iii) oxidation of metal-catechol complexes by dissolved oxygen, resulting in the formation of insoluble polymers.

The first step consists in a fast, heterogeneous redox reaction that occurs as soon as catechol is added to the soil slurry. It takes place to the same extent under nitrogen and oxygen sparging and occurs simultaneously with the second step, i.e. with the formation of catechol-metal complexes. This step is associated with an outburst in iron and manganese release into the solution. Under nitrogen sparging, a stable situation is reached in terms of catechol, iron, and manganese concentration levels.

In the presence of oxygen, and once the first two steps have taken place, catechol consumption proceeds, according to the third, homogeneous step, independently of the presence of soil. Since all metal released in solution is complexed by catechol, the breaking-down of the metal-catechol complexes by molec-

ular oxygen and polymer formation occur simultaneously. The metal ions released by oxidized products are complexed again and again, as long as catechol is present at sufficiently high concentration levels. Then, complexed iron and manganese concentration progressively decrease along with catechol removal.

These phenomena take place with a variety of different soil samples of broadly diverse physico-chemical characteristics, coming from different nations within and without the Mediterranean area.

This suggests that an extremely simple de-phenolisation treatment can be set up with a stirred and aerated vessel, where OMW can be put into contact with a soil slurry. The soil can be excavated on the spot.

The experimental results reported in this work suggest that iron-catecholate and manganese-catecholate complexes formed in the second step play a fundamental role in the natural degradation reactions which occur when *o*-diphenol-contaminated waters are spread onto soil, according to a common practice followed in most olive oil producing countries. Such a mechanism should be taken into account when considering natural and enhanced attenuation of phenol-polluted groundwater.

Acknowledgments

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