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Role of the caffeic acid oxidation products on the iron mobilization at the soil-root interface

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Previous results show that the reduction of Fe(III) by caffeic acid (CAF) is strongly influenced by the pH of the reaction medium (DEIANA et al., 1995). In particular, it has been found that at pH > 3.8 the reducing activity of CAF towards the Fe(III) ions in solution is low, but it increases when Fe(III) is complexed as Fe(III)-polygalacturonate. The mobilization of the Fe(II) ions, which form upon the Fe(III) reduction, has been shown to depend mainly on the nature of the Fe(II)-polygalacturonate complexes (DEIANA et al., 1994a). In particular, it has been observed a high redox activity of CAF towards Fe(III) when the metal ion is coordinated by the carboxylic groups of the macromolecule. The Fe(III) reduction has been found to decrease when an oxydrilic group was inserted in the Fe(III) coordination sphere. The Fe(II) produced partly diffuses into the external solution and partly is still strongly held by the polysaccharidic matrix. The oxidation of CAF by Fe(III) gives rise to the formation of products (OP) with different polymerization degree, some of which are similar to those found in natural systems (DEIANA et al., 1994b). In order to determine the role of these products in the Fe(III) reduction as well as in the mobilization of the Fe(II) produced it was set up an electrochemical method to synthesize these products (DEIANA et al., 1994b). Here are reported some results about the interaction which establish between the CAF oxidation products and iron in both oxidized and reduced form.

Materials and methods

The Fe(II) determination, HPLC analyses and electrochemical oxidation of CAF were performed according to the procedures reported by DEIANA et al. (1994b; 1995). Kinetic measurements were carried out at room temperature, under argon, on systems with 0.6 mM initial concentration of oxidation products and different amounts of Fe(III) and Fe(II), by monitoring the Fe(II) and OP contents.

Results and discussion

Figure 1 shows, as an example, the chromatographic profile of the products obtained via electrochemical oxidation of CAF. The reaction between these products and Fe(II) was studied as a function of time at pH 3.0, 4.5 and 5.2, and at a metal/OP molar ratio equal to 2. The UV/VIS spectra in the 300-800 nm range are characterized by the presence of two absorption bands at 320 and 680 nm: the former is attributable to structures which maintain the typical conjugation of CAF and the latter to a complex formed by Fe(II) and the CAF oxidation products, where are probably involved the -OH phenolic groups of the condensed structures. The concentration of the complexed species increases as pH increases, as evidenced by the increase in the band at 680 nm. The UV/VIS spectra of CAF and Fe(II) solutions, carried out in the same analytical conditions, do not show absorption bands in the 400-800 nm range, so that the involvement in the complexation process of the biomolecule present in the reaction mixture (4%) can be excluded. It is important to point out that such complexes tend to precipitate with time and that this reaction is strongly active at pH 5.2 (Fig. 2). The chromatographic tests show that at pH 4.5 the compounds 4, 5 and 7 are mainly responsible for the precipitation process, whereas at pH 5.2 the compounds 6, 3 and 2 are involved, too. The precipitation process can be attributed to the reticulation of different compounds by Fe(II) ions, which leads to the formation of a polymeric matrix where CAF can be trapped, too, as shown by the HPLC tests. The polymeric structure is confirmed by the IR spectra of the precipitate which are similar to those of natural humic acids. They suggest that also the carboxylic groups are involved in the Fe(II) ion complexation. The composition of the precipitate is under study.

The interaction between the CAF oxidation products and the Fe(III) ions was studied at pH 2.5, 3.0 and 4.5 on systems having different Fe(III)/OP ratios (from 1.0 to 9.0), the oxidation product concentration being kept constant. The redox reaction was found active at pH 2.5; it proceeds through two steps: the former is fast and leads to the release of 4 electrons, the latter is slower and involves the release of only 1.2 electrons. At pH 3.0 the same stoichiometry was evidenced, but the kinetics of the redox reaction was found slower. This behaviour differs from that previously defined for the Fe(III)-CAF system, where a release of 9 electrons for one molecule of CAF oxidized has been shown (DEIANA et al., 1992). Such a difference is partly attributed to the release of two electrons which accompanies the formation of the OP via the CAF electrochemical oxidation. The lack of other 2 electrons suggests that a fraction of the -OH phenolic groups are involved in the polymerization process which leads to the formation of compounds

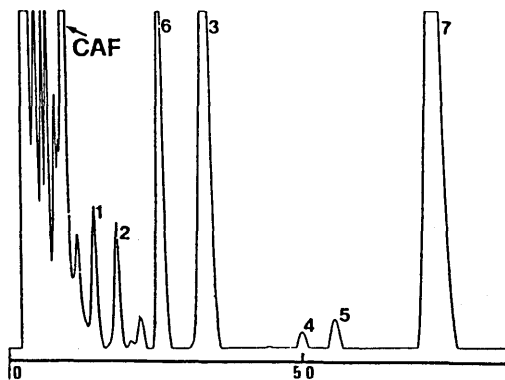


Figure 1. Chromatograms relative to the system at pH 3.0 recorded at 290 nm. Starting conditions: 2.1mM CAF: 1 M NaClO₄ : 1M CH₃COOH.

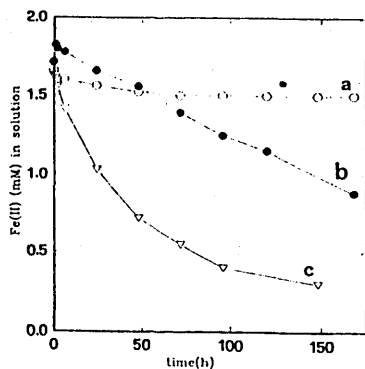


Figure 2. Fe(II) (mM) in solution as a function of time at pH 3.0 (a), pH 4.5 (b) and pH 5.2 (c). The initial OP concentration was 0.6 mM.

with a molecular weight higher than that of CAF as well as Fe(III)-OP complexes, as shown by the UV/VIS spectra. At pH 4.5 no Fe(II) formation was recorded. As evidenced by the UV/VIS spectra, this can be attributed to the formation of Fe(III)-OP polymers which tend to precipitate with time and with increasing the Fe(III) concentration. The IR spectra indicate that also the Fe(III)-OP precipitates have a polymeric structure. The chromatographic tests show that for Fe(III)/OP ratios equal to 1, 2 and 5, all the products are involved, particularly those with a retention time higher than 50 min; whereas those with a retention time lower than 50 min disappear at a Fe(III)/OP ratio equal to 9.

Conclusions. The results show that the CAF oxidation products at the soil-root interface are able:

- to operate the reduction of Fe(III) to Fe(II) ions at low pH values;
- to form Fe(III)-polymers, thus preserving the Fe(III) ions from reduction;
- to form insoluble Fe(II)-polymers, thus limiting the Fe(II) diffusion towards the absorbing cells.

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