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ROLE OF THE POLYGALACTURONATE NETWORK ON THE IRON (III) REDUCTION BY CAFFEIC ACID.

C.Gessa*, S.Deiana**, G.P.Lauro**, M.Marchetti*** and M.Usai**

*Istituto Chimica Agraria, Universtà di Bologna; **DI.S.A.A.B.A., Università di Sassari; ***I.A.T.C.A.P.A. del C.N.R., via Vienna 2 Sassari.

The complexing capacity of the "mucigel" is ascribed to polysaccharide acids organized in a fibrillar structure. Gessa C. and Deiana S. (140: 1-13, 1992a; 1992b) using a network of Polygalacturonate with a fibrillar structure similar to that found in the real systems, have shown that the mobility of metal ions depends on their affinity for the functional groups of the polysaccharide.

The availability of the immobilized ions for the absorbing cells is mediated principally by organic molecules with low molecular weight having complexing or reducing capacity. Among these substances caffeic acid (CAF) play an important role in the transport of the iron from soil to plasmalemma. Deiana S. et al., (1992) Gessa C. et al., (1992) studied the iron(III)-CAF system in aqueous solution defining the stoichiometry and suggesting the probable mechanism of the redox reaction.

This communication reports the role of polygalacturonate network on the Fe(III) reduction by caffeic acid. The effect of phosphate ions on the redox reaction is also considered.

EXPERIMENTAL

Systems containing CAF, phosphate ions and iron (III)-polygalacturonate network were prepared by mixing the solutions and suspension previously brought up to the working pH. The reaction volume was 100 mL. Iron(II) was determined as 1-10-phenantroline complex in a small volume of solution buffered by acetate at pH 4,5. The HPLC tests were performed according to Deiana et al (1992). The Fe(III)-networks were prepared treating Ca(II)-networks with a solution of Fe(III) and D-galacturonic acid in a molar ratio of 5 at pH 3.5. The Fe(III)-networks were dialyzed several times with distilled water.

RESULTS AND DISCUSSION

To determine the role of the polygalacturonate network in presence and in absence of phosphate ions on the redox reaction, two systems were studied at pH 4 and 5. The system 1 was composed of a network reticulated with 58 μ moles of Fe(III) and 16.726 μ moles of CAF; the system 2 of 70.13 μ moles of Fe(III), 24.129 μ moles of CAF and 73.13 μ moles of phosphate. Table reports, the percentage of the Fe(II) and Fe(III) released in the external solution after 48 hours of reaction, of exchangeable (e) and immobilized (R) by the organic matrix; the yield of Fe(II) relative to the binary (Fe(III)-CAF) and ternary (Fe(III)-CAF-Phosphate) systems are also reported. The results show that the redox reaction is much more active in system 1 and 2 in respect to the aqueous binary and ternary systems, in fact only 9% and 2% of the reticulating iron is reduced in these last two. The presence of phosphate ions inhibits the reduction reaction inside the network.

These aspects can be explained as following:

- a) high stability of the Fe(III)-polygalacturonate complex where the Fe(III) is preserved to the hydrolysis reactions;
- b) the stability of the Fe(III)-network was increased when phosphate occupies the active site of the redox reaction

Fe(III)-Network-CAF (System 1)								Fe(III)-CAF
pH	CAF ^a	n.e ⁻	Liquid phase		Solid phase			Fe(II)
			Fe(II)	Fe(III)	Fe(II) _e	Fe(III) _e	Fe(III) _R	
4.0	8.40	4.70	20.90	5.45	51.35	22.30	0.00	9.30
5.0	6.64	4.30	5.10	4.03	43.90	30.00	16.97	8.90

Fe(III)-Network-CAF-P (System 2)								Fe(III)-CAF-P
pH			Liquid phase		Solid phase			Fe(II)
			Fe(II)	Fe(III)	Fe(II) _e	Fe(III) _e	Fe(III) _R	
4.0	5.01	4.94	5.25	0.81	30.10	0.00	58.74	2.50
5.0	5.56	3.30	2.70	1.40	23.40	0.00	72.50	2.40

The amount of the iron and caffeic acid inside the network was determined by treating the solid phase with 0.1 M NaClO₄ solutions. P: Phosphate; CAF^a: mmoles of reacted caffeic acid; n.e⁻: Fe(II)/CAF^a.

Some notes are to lay stress on:

i) The intermediate product I present in aqueous systems (Deiana S. et al., 1992) is not detected either in the external liquid phase and in the network "free space", probably due to its instability inside the matrix; ii) the intermediates A and B are present in "free form" either in the external solution or in the network "free space".

These data indicate that, in the redox process, is active only the first step of the mechanism previously reported (Deiana S. et al., 1992).

The reduction of the iron restore the fibrillar structure of the system 1 which appears collapsed in the Fe(III)-Ca(II)-polygalacturonate. This arises from two distinct mechanisms of interaction of Fe(II) and Fe(III) with the functional groups of the fibrils: electrostatically with Fe(II) and covalently with Fe(III).

The regenerate fibrillar structure appears shrunk respect to the Fe(II)-network prepared treating Ca(II)-network with Fe(II) solutions. The mechanism of this phenomenon which appears to be related to the accumulation of CAF inside the fibrils as well as the effect of the phosphate ions on the physical properties of network is under study.

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