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TRANSFER OF METAL IONS IN THE SOIL-ROOT INTERFACE: INFLUENCE OF COPPER(II) ON THE STABILITY OF THE FIBRILS.

C.Gessa and S.Deiana
Istituto di Chimica Agraria dell'Università di Sassari

A network of Ca-polygalacturonate arranged in fibrils similar to those of plant roots (Gessa C. and Deiana S., (1990); C.Gessa and Deiana S., (1990)) constitutes a very useful model for the study of the ionic transfer both in the soil-root interface and in the apoplast.

Due to the fact that important properties of the network, such as the hydration degree and the absorption phenomena, vary dramatically with the reticulating ion (Gessa C. and Deiana S., (1989)), this note reports on the influence of the metal ions on the fibrillar structure of the network and gives further information about the transfer of the metal ions to the roots.

Experimental

The absorption tests were carried out by treating the Ca-network with 12 mM $CaCl_2$ solutions containing varying amount of $CuCl_2$ until the equilibrium was reached. The two ions present in the external liquid phase, in the free space volume and complexed by the organic matric were determined by using a plasma emission spectrometer and an electro-chemical analyzer. Electron-micrographs were made by scanning electron microscopy (SEM).

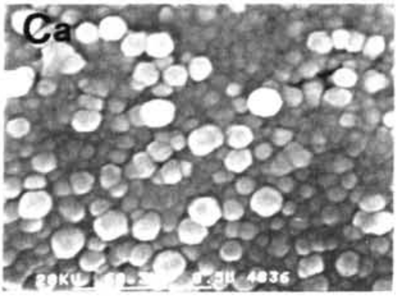
SEM was performed on samples as follws:

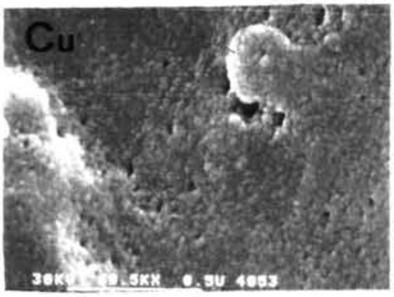
a) treatment with glutaraldehyde (2.5%) in buffer solution (pH 7) for 4 hours at 4°C;
b) fixation with the same buffer solution containing OsO_4 (1%) for 2 hours at 4°C;
c) washing with the buffer solution and distilled water;
d) dehydration with acetone;
e) drying and gold metallization.

Results and discussion

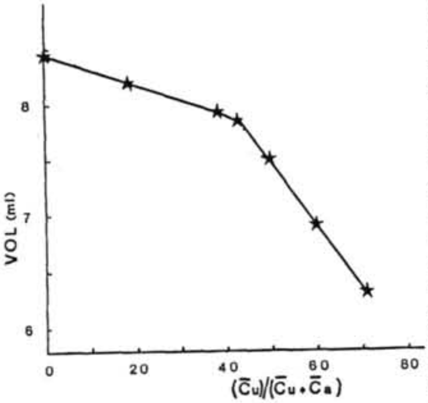
Previous results have shown that the physical and chemical properties of the network are closely related to the reticulating ion and this suggests that the arrangement of the fibrils could be altered following the substitution of Ca(II) ions with metal ions such as Cu(II),VO(IV),Fe(III) and Al(III).

Scanning electron micrographs showing the surfaces of the Ca, and Cu-network are reported in fig.1. They show the collapse of the fibrillar structure if Ca(II) ions are exchanged with Cu(II) ions. The two reticulating ions behave very differently due to their different type of interaction with the organic matric; Ca(II) forms outer-sphere complexes, whereas Cu(II) forms inner-sphere complexes.

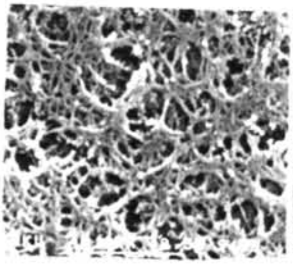




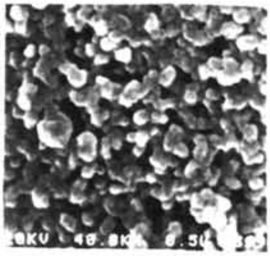
To have a better understanding of the influence of the stability of the fibrils, we synthesized several networks wich contain both Ca(II) and Cu(II) ions in different ratios. The hydration degree of the Cu-Ca-polygalacturonate versus the ionic molar fraction of Cu(II) in the network is plotted in fig.2. The hydration degree - that is the volume of the network- decreases slowly as the amount of reticulating Cu(II) increases. A dramatic reduction of the volume is observed at Cu(II) content higher than 40% suggesting that the fibrillar structure of the network becomes unstable when the percentage of reticulating Ca(II) is lower than about 60%. This is confirmed by the scanning electron micrographs which reveal the persistence of a partially dehydrated fibrillar structure in the network containing 20% Cu(II) (fig.3A). This type of structure is destroyed at 45% Cu(II) (fig.3B) and cannot be restored by treatment with calcium solutions (fig.3C).



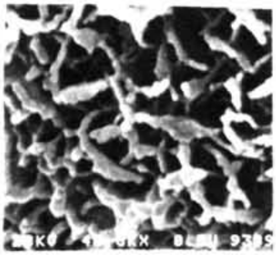
3A



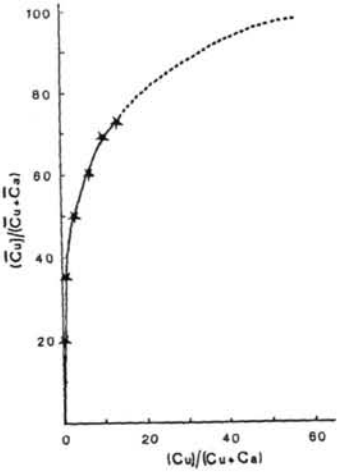
3B



3C



The distribution of Cu(II) and Ca(II) ions in the network, as a function of the molar fraction of Cu(II) in the equilibrium solution, is shown in fig.4. The affinity of the Cu(II) to the polygalacturonate is so high that, at very low concentration in solution, this ion can be considered totally complexed by the polymer.



The Cu(II) molar fraction in the soil liquid phase is usually very low, therefore this metal, and others such as Fe(III) and Al(III), which have a strong affinity to the root mucilages, cannot diffuse either in the soil-root interface or in the apoplast, and their transfer towards the absorbing cells is controlled by soluble organic ligands, originating either in the rizosphere and in the plant roots.

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