Geophysical Research Abstracts,
Vol. 11, EGU2009-6780, 2009
EGU General Assembly 2009

Accumulation of metal ions by pectinates

S. Deiana (1), L. Deiana (2), A. Palma (3), A. Premoli (1), and C. Senette (1)

(1) University of Sassari, DISAABA, Sassari, Italy (sadeiana@uniss.it), (2) Dipartimento di Chimica, Via Vienna 2, 07100 Sassari, Italy, (3) CNR, Istituto di Scienze delle Produzioni Alimentari, Sezione di Sassari, Via dei Mille 48, 07100 Sassari, Italy

The knowledge of the mechanisms which regulate the interactions of metal ions with partially methyl esterified linear polymers of α-1,4 linked D-galacturonic acid units (pectinates), well represented in the root inner and outer apoplasm, is of great relevance to understand the processes which control their accumulation at the soil-root interface as well as their mobilization by plant metabolites.

Accumulation of a metal by pectinates can be affected by the presence of other metals so that competition or distribution could be expected depending on the similar or different affinity of the metal ions towards the binding sites, mainly represented by the carboxylate groups.

In order to better understand the mechanism of accumulation in the apoplasm of several metal ions, the sorption of Cd(II), Zn(II), Cu(II), Pb(II) and Cr(III) by a Ca-polygalacturonate gel, used as model of the soil-root interface, with a degree of esterification of 18% (PGAE1) and 65% (PGAE2) was studied at pH 3.0, 4.0, 5.0 and 6.0 in the presence of $CaCl_2$ 2.5 mM..

The results show that sorption increases with increasing both the initial metal concentration and pH. A similar sorption trend was evidenced for Cu(II) and Pb(II) and for Zn(II) and Cd(II), indicating that the mechanism of sorption for these two ionic couples is quite different. As an example, at pH 6.0 and an initial metal concentration equal to 2.0 mM, the amount of Cu(II) and Pb(II) sorbed was about 1.98 mg^{-1} of PGAE1 while that of Cd(II) and Zn(II) was about 1.2 mg^{-1}.

Cr(III) showed a rather different sorption trend and a much higher amount (2.8 $mg^{-1}$of PGAE1 at pH 6.0) was recorded. The higher affinity of Cr(III) for the polysaccharidic matrix is attributable to the formation of Cr(III) polynuclear species in solution, as shown by the distribution diagrams obtained through the MEDUSA software.

On the basis of these findings, the following affinity towards the PGAE1 can be assessed: Cr(III) $>$ Cu(II) $\approx$ Pb(II) $>$ Zn (II) $\approx$ Cd(II).

Surprisingly, simultaneous sorption tests and SEM analyses indicate that a different mechanism regulates the sorption of Cu(II) and Pb(II) by PGAE1. In fact, the amount of Pb(II) sorbed (0.92 μmoles $mg^{-1}$of PGAE1) by PGAE1 was nearly independent by the presence of Cu(II) ions, at least at the three different concentrations tested, that indicates a higher affinity of Pb(II).

Such an aspect was further confirmed by exchange experiments. Samples of PGAE1 saturated with 1.96 μmoles $mg^{-1}$of Cu(II) or 2.01 μmoles $mg^{-1}$of Pb(II) were put in contact with 100 mL of solutions containing 97.3 μmoles of Pb(II) or 99.4 μmoles Cu(II), respectively. The exchange kinetics show that about 80% of Cu(II) was stochiometrically exchanged by Pb(II). In contrast, only about 10% of Pb(II) complexed by PGAE1 was exchanged by Cu(II).

The kinetics of simultaneous sorption of all the metal ions tested indicate that Pb(II) is selectively sorbed by the PGAE1 gels. Cd(II) and Zn(II) show a similar affinity towards PGAE1. Thus, in the simultaneous presence of these ions, their selectivity towards this matrix follows the order: Pb $>$ Cu $>$ Cd $\approx$ Zn. Sorption of Cr(III) in the presence of the ions considered was not possible to carry out due to interference phenomena.

The sorption of the same ions by 50 mg of PGAE2 evidences that the amount of Cu(II), Pb(II), and Cr(III) sorbed is markedly lower than that found for PGAE1. By considering that two carboxylic groups are involved in the complexation of a metal ion, the data show that such a stoichiometry is respected only for Pb(II). The amount of Cu(II) sorbed is about 50% lower than that of Pb(II) at all the pH values tested whereas those of Zn(II) and Cd(II) are negligible whereas that of Cr(III) is the highest. The different behaviour of Cu(II) compared to Pb(II) can be explained taking into account for both hydrophobic and steric effects of the methyl groups as well as to their different charge density. Thus, it can be concluded that the accumulation of metals at the soil-root interface strictly depends on the esterification degree of the root pectinates which, even highly esterified, do not loose the ability to accumulate metals, mainly Pb(II) and Cr(III).