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Nickel sorption capacity of ground xylem of *Quercus ilex* trees and effects of selected ligands present in the xylem sap

Geórgia C.L. Araújo[a,*], Sherlan G. Lemos[b], Cristina Nabais[c]

[a]*Escola de Artes, Ciências e Humanidades da Universidade de São Paulo, Av. Arlindo Bettio, 1000, Ermelino Matarazzo, 03828-000 São Paulo, SP, Brazil*
[b]*Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676, 13560-970 São Carlos, SP, Brazil*
[c]*Centro de Ecologia Funcional, Departamento de Botânica, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3000 Coimbra, Portugal*

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Summary

In this work the influence of four different ligands present in the xylem sap of *Quercus ilex* (histidine, citric, oxalic and aspartic acids) on Ni(II) adsorption by xylem was investigated. Grinded xylem was trapped in acrylic columns and solutions of Ni(II), in the absence and presence of the four ligands prepared in KNO_3 0.1 mol L^{-1} at pH 5.5, were percolated through the column. Aliquots of solutions were recovered in the column end for Ni determination by graphite furnace atomic absorption spectrometry (GFAAS). The experimental data to describe Ni sorption by xylem in both the presence and absence of ligands was better explained by the Freundlich isotherm model. The decreasing affinity order of ligands for Ni was: oxalic acid > citric acid > histidine > aspartic acid. On the other hand, the Ni(II) adsorption by xylem increased following the inverse sequence of ligands. Potentiometric titrations of acidic groups were carried out to elucidate the sorption site groups available in *Q. ilex* xylem. The potentiometric titration has shown three sorption sites: pK_a 2.6 (57.7% of the sorption sites), related to monobasic aliphatic carboxylic acids or nitrogen aromatic bases, pK_a 8.1 (9.6%) and pK_a 9.9 (32.7%), related to phenolic groups.

Abbreviations: GFAAS, graphite furnace atomic absorption spectrometry; SC, sorption capacity; SC_{exp}, experimental sorption capacity.

*Corresponding author. Tel.: +55 11 30911020.
E-mail address: georgialabuto@usp.br (G.C.L. Araújo).

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Introduction

In trees, long-distance transport of elements absorbed from the soil occurs through the xylem vessels (Marschner, 1995). Although the mechanism of solute transport is predominantly by mass flow in the non-living xylem vessels, important interactions occur between solutes and the cell walls of the vessels (Wolterbeek et al., 1984). The metal-binding capacity of the cell walls seems to be related to the contents of their main biopolymer, namely cellulose microfibrils, hemicellulose, pectins and lignin. The basic structural unit of pectins, α-D-polygalacturonic acids, is rich in negatively charged free carboxylic groups (Läuchli, 1976). The interactions between cations and the negatively charged groups in the cell walls can delay the ion translocation in the xylem vessels (Van de Geijn and Petit, 1979). The level of interaction depends on the valency of the cations, their concentration, competing cations, complexing agents, charge density of the negative groups of the cell wall, diameter of the xylem vessels and the pH of the xylem sap (Marschner, 1995). The knowledge of how trace elements are transported in the xylem sap and its interactions with the xylem walls and ligands has important implications in the physiology of plants exposed to trace metals (Mihucz et al., 2000). Also, the understanding of the behavior of lignocellulosic materials as biosorbents of toxic metals can have potential applications in environmental technologies.

Serpentine-derived soils are known to be unfavorable to plant growth and productivity due to the presence of high concentrations of Ni (Proctor, 1999). Holm oak (*Quercus ilex*) is the dominant tree growing on serpentine soils of north-east Portugal (Sequeira et al., 1991). Roots of *Q. ilex* growing on serpentine soils are then exposed to high levels of Ni that can be mobilized and transported in the xylem sap. *Q. ilex* trees growing on the serpentine soils showed higher concentrations of Ni in wood and inner bark, compared with trees from a non-serpentine soil, although leaves from both sites showed similar concentrations of Ni (Nabais, 2000). During the long-distance transport in the xylem vessels, substances present in the xylem sap can become involved in processes of adsorption to charge sites present in the cell walls. These processes can reduce the amount of substances, such as Ni, that can reach the leaves.

Upon exposure to excessive metal availability, plants appear to increase the syntheses of a variety of metal-chelating compounds, such as amino acids (nitrogen donor ligands) (Krämer et al., 1996), carboxylic acids (oxygen donor ligands) (Cocker et al., 1998) and phytochelatins (sulfur donor ligands) (Chen et al., 1997; Ma and Miyasaka, 1998). Besides, the presence of sideropheres could promote metal chelation and transport in the xylem sap (Sally and Neilands, 1981). Although chelating agents can increase the translocation of trace metals in the xylem vessels, they are also able to keep the free trace metal ions within certain limits, thus reducing their toxicity (Salt et al., 1995). Like most transition metal ions, nickel forms complexes with several organic substances (Tiffin, 1971; Pohlmeier, 1999; Zeller and Feller, 1999). Among the compounds that are involved in the chelation of Ni are citrate, malate (Still and Williams, 1980; Yang et al., 1997; Lee et al., 1998), histidine (Krämer et al., 1996) and nicotianamine, a non-protein amino acid (Callahan et al., 2006; Mari et al., 2006).

In this work, we investigate the interaction between Ni and grinded xylem of *Q. ilex* in the presence and absence of several organic ligands. The quantity of adsorbed Ni and its concentration in equilibrium was calculated using Langmuir, Freundlich, Sips and BET isotherm models. These isotherms can provide information about the sorption capacity (SC) and the preference of each studied ligand for Ni. Additionally, potentiometric titrations of acidic groups were carried out to elucidate the available sorption sites of the grinded xylem.

Materials and methods

Materials

A 650 freezer Mill (Spex CertiPrep, USA) was used to grind *Q. ilex* L. (Holm Oak) xylem. The xylem recovered from flow studies was lyophilized using an E-C Micromodulyo (Edwards, England). An instrument GF AAS AA100 (Perkin Elmer, USA) equipped with an autosampler AS-72 (Perkin Elmer, USA), pyrolytically coated graphite tubes with L'vov platform and deuterium lamp as background corrector was used for Ni determinations performed at 232.0 nm with a slit width of 0.2 nm. A digital potentiometer (Metrohm, 716 DMS Titrino, England) and a glass-combined electrode were used for pH adjustment and for potentiometric titrations. In the flow analysis a peristaltic pump (model Minipuls 3, Gilson, USA) and acrylic columns closed with 90-μm porosity filters (MoBitec, Germany) were used. Isotherms data analyses were performed employing the Sigma Plot 8.0 software (Statistical Solutions, USA).

Nickel solutions were prepared from dilutions of a 1000 mg L^{-1} stock (Titrisol®, Merck, Germany) in 0.1 mol L^{-1} KNO_3 (Merck, Germany) medium at pH 5.5. These conditions were chosen since they correspond to average values of ionic strength and pH of *Q. ilex* xylem