Experimental study of the ternary system uranyl(VI) – synthesized fulvic acid – H_2O as a function of pH, using ESI-MS and optical spectroscopies (UV-visible, ATR-FTIR) at 25°C, 0.1 MPa

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The knowledge of the chemical reactivity of the hydrophilic organic compounds and radioelements in a wide pH range and particularly in highly basic solutions is fundamental for a better understanding and modelling of radioelements release from irradiated waste tanks surrounded by concretes and stored in deep underground vaults in contact with oxidizing natural waters. Previous works have reported that fulvic acid is a main product of the reaction of natural organic matter with alkaline solutions. The synthesis of fulvic acid was realized in weak basic solution (pH = 8-10) under highly oxidizing conditions, and interactions of uranyl (VI) and fulvate anions have been investigated in acidic and neutral solutions. In contrast, reliable data of reactions of uranyl (VI) and fulvate anion in alkaline solutions appear to be lacking.

The goal of the present study is (1) to synthesize fulvic acid in highly alkaline solution (pH = 13), (2) to detect the presence of uranyl(VI)-fulvate aqueous complexes, (3) to determine their number and (4) to evaluate their equilibrium quotient (log Q) in $NaNO_3$ solutions.

Fulvic acid has been synthesized for the first time, using the reaction of catechol ($C_6H_4(OH)_2$) and acetic acid (CH_3COOH) at pH = 13 and under ambient condition. Synthesized fulvic acid has been used as initial compound in the experimental study of the ternary system U(VI) – synthesized fulvic acid – H_2O as a function of pH (4 - 12). UV-visible absorption measurements of a 10^{-3} M U(VI) solution containing 200 $mg.L^{-1}$ synthesized fulvic acid have revealed for the first time the presence of a uranyl(VI)-fulvate aqueous complex at pH values up to 12. The formation of a uranyl(VI)-fulvate complex at such high pH values where only uranyl(VI) hydrolyzed ($UO_2(OH)_4^{2-}$) and/or uranyl(VI) carbonate ($UO_2(CO_3)_4^{2-}$) species could be stable proves that fulvic acid is among the strongest complexing agents of uranyl(VI) ion over a wide pH range (4 – 12).

Bioaccumulated manganese and nickel in endemic plants from New Caledonian mining soils

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New Caledonian ferritic soils (more than 50 % of iron) are naturally rich in metals (chromium, nickel, cobalt, and manganese), deficient in major nutrients (nitrogen, phosphorous, and potassium), and unbalanced for the calcium/magnesium ratio. Under these particular ecological conditions, New Caledonia, recognized as a hot-spot of biodiversity, is a natural laboratory to study and understand the adaptation strategies of plants to metalliferous soils, and particularly the tolerance and (hyper)accumulation of metals by plants. Moreover, understanding such mechanisms is essential to develop rehabilitation or phytoremediation techniques for soils, as well as phytomining techniques.

Thus, in order to understand the adaptation of plants to such metalliferous soils, several plant species of two endemic and frequent plant genera were collected in an ultramafic and future nickel-mining massif of New Caledonia: *Tristaniopsis guillainii* and *T. calobuxus* (Myrtaceae), and *Phyllanthus serpentinus* and *P. favieri* (Euphorbiaceae), because of their nickel and/or manganese accumulating or hyperaccumulating nature. Next, a series of characterization techniques were adapted and then coupled to cryogenics. The combined use of those multiple techniques (cryo-microtomy, cryo-SEM, µXRF, cryo-XAS, and soil characterization) allowed to study co-location and speciation of nickel and manganese in the different plant organs and soils (rhizospheric and bulk).

Bioaccumulated nickel and manganese had different distribution patterns. In leaves, Ni accumulated in non photosynthetic tissues whereas Mn preferentially accumulated in mesophyll whatever the plant species. Nevertheless, in spite of a different speciation in soils, nickel and manganese were both found as similar divalent organometallic complexes in the different plant parts.