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Progressing from Terra Preta de Índios to the Whole World

Selective extraction of the characteristic humic fraction from *Terras Pretas de Índios*

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Introduction

The *Terra Preta de Índios* soils, found in the Amazon basin differ markedly from adjacent soils, because of their higher fertility and greater carbon content. This high fertility and the great capacity of these soils to maintain it, despite their intensive and degradative use (resilience), can be explained by its high levels of organic matter with a strong pyrogenic character.

In this way, these soils provide us an excellent model that helps pursue the goal of improving soil fertility and promoting soil carbon sequestration. In spite of the big efforts to reproduce these soils, there are no analytical methods to check the success of these attempts.

Studies employing Nuclear Magnetic Resonance (NMR) and Multivariate Curve Resolution (MCR) showed that humic acids from *Terra Preta de Índios* can be satisfactorily modelled as a binary mixture [1].

One of the components of this mixture is similar to regular humic acids from tropical soils. It presents signals of the following chemical groups: alky, N-alkyl, methoxyl, carbohydrates, aryl, O-aryl, aliphatic carboxyl and amide. These chemical groups indicate the presence of plant material (fat acids, proteinaceous material, lignin and cellulose) in different humification stages.

The second component is characterised by condensed aromatic structures with high charge density due to carboxylic groups linked directly to the aromatic core, i.e., pyrogenic carbon (biochar) partially oxidised. This structure, recalcitrant and reactive, is what explains the high fertility and resilience of these special soils.

Taking this in account, it is proposed a modification of the classical extraction method of the International Humic Substances Society seeking to extract selectively the recalcitrant and reactive fraction of the soil organic matter that differentiates *Terras Pretas de Índios* from regular soils. This modification consists in extracting exhaustively the humic fractions in a sequence of base (0.1 M NaOH) adjusted to pH 7, to pH 10.6, and at pH 12.6. The afterwards obtained samples is analysed by solid state ^{13}C Nuclear Magnetic Resonance.

Variable-amplitude cross-polarization (VACP) Solid-state ^{13}C NMR experiments were carried out using a 500 MHz Varian spectrometer at ^{13}C and ^{1}H frequencies of 125 and 500 MHz, respectively. Magic-angle spinning (MAS) at 15 kHz was employed. Typical cross-polarisation times of 1 ms, acquisition times of 13 ms, and recycle delays of 500 ms were used. High-power Two-Pulse Phase-Modulation (TPPM) proton decoupling of 70 kHz was applied in all experiments.

Results and Discussions

The experimental NMR spectra of humic acids, extracted by aqueous NaOH solutions at pH 7 and 10.6, were very similar to the second component spectra, estimated by mathematical method (MCR). These spectra are characterised by a featureless aryl peak centred at 129 ppm, typical of a polycondensed aromatic structure and by a carboxyl peak with a clear up field shift (168 ppm), attributable to carboxyl groups that are attached directly to the aromatic backbone.

The fact that the simulated spectrum from MCR method represents a real component of the soil organic matter from *Terra Preta de Índios,* corroborates the results, obtained by the MCR analysis, in the characterisation and quantification of the distinctive humic fraction from *Terras Pretas de Índios* [1].

These results confirm the precision and accuracy of the MCR, as well as the suitability of the proposed extraction method.

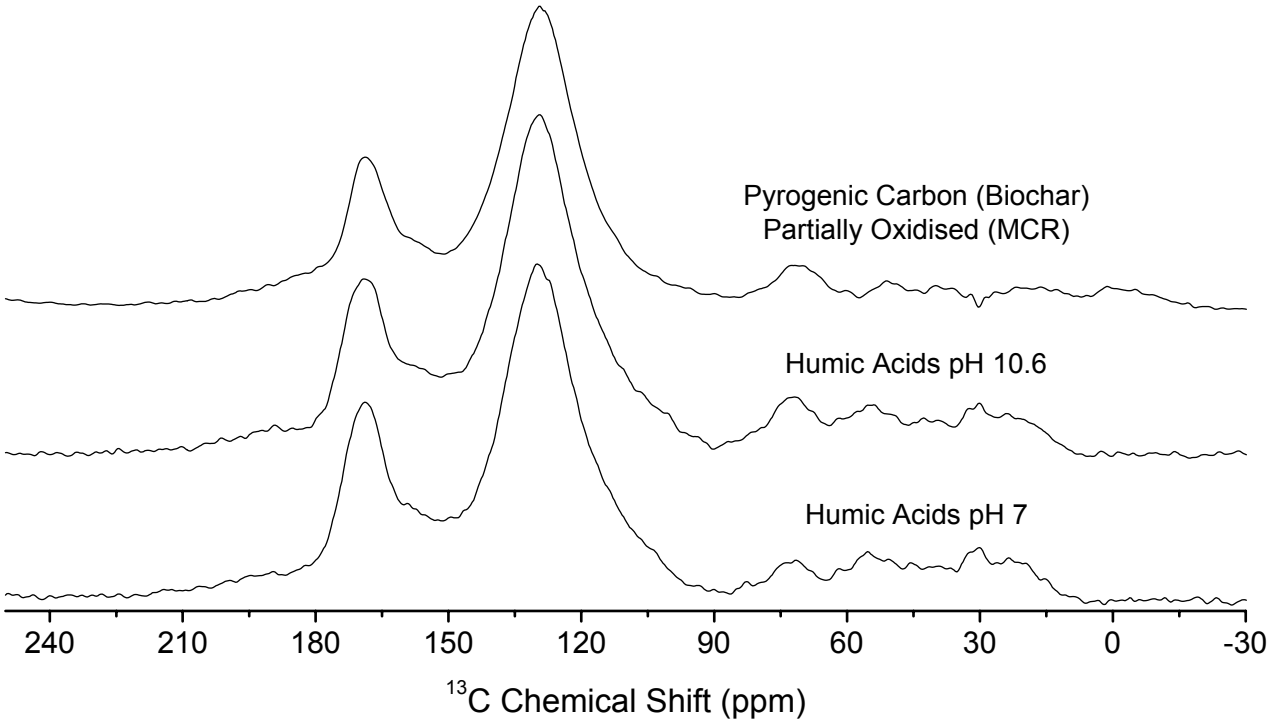

Figure 1. Solid State ^{13}C NMR of the characteristic humic fraction from *Terra Preta de Índios* and the simulated spectra obtained by MCR.

Conclusions

The aqueous NaOH solutions, adjusted at pH 7 and at pH 10.6, selectively extracted the distinctive humic fraction of *Terra Preta de Índios* soils, *i.e.*, polycondensed and functionalised aromatic structures. In this way, this approach can be used as a rapid and simple method to evaluate the proposals to reproduce the *Terra Preta de Índios* soils.

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[1] Novotny, E.H.; Hayes, M.H.B.; Madari, B.E.; Bonagamba, T.J.; Deazevedo, E.R.; Desouza, A.A.; Song, G..; Nogueira, C.M; Mangrich, A.S. 2009. Lessons from the Terra Preta de Índios of the Amazon Region for the Utilisation of Charcoal for Soil Amendment. *J. Braz. Chem. Soc.*, 20, 1003-1010.