

Chemical functionalisation of activated charcoal - Reproducing the *Terra Preta de Índios* organic matter model

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Introduction

Terras Pretas de Índios are anthropogenic soils found in the Amazon which have high carbon content, high fertility and high resilience. These characteristics are due to the pyrogenic character of their organic matter.

Based on several investigations of the organic matter from *Terra Preta de Índios*, an efficient model of organic material has been proposed, that can provide agriculture sustainability and carbon sequestration. This model involves a compound of polycondensed aromatic structures with carboxylic functionality.

Charred materials have condensed aromatic groups that guarantee their recalcitrance in the environment (half-life ranging from centuries to millennia), being so an efficient material for carbon sequestration. Its application in the soil is followed by biological and chemical transformations through which carboxyl groups are directly connected to the recalcitrant aromatic structures. After those transformations, the final compound attributes high fertility to the soil. This is what makes *Terra Preta de Índios* soils so fertile, differentiating them from other soils in the Amazon.

However, this transformation process may take decades to occur in nature. That is why, through chemical functionalisation of charcoal, we are seeking to obtain, in a short period of time, compounds similar to the ones found in the *Terra Preta de Índios*, which sequester carbon in a recalcitrant and reactive form.

To promote the oxidation of peripheral aromatic units to carboxylic groups, activated charcoal was subjected to chemical treatments with different concentrations of NaOCl (0.05; 0.1 and 0.2 M). Then, the obtained mixture was

filtered and acidified to pH ~ 1. The humic acid like fraction precipitated and the fulvic acid like fraction remained in solution. Thereupon, the humic acids were recovered by centrifugation and dialysed; and the fulvic acids were purified with resin XAD-7 and Ambertile IR-120. Afterwards, both fractions were freeze dried.

Variable-amplitude cross-polarization (VACP) Solid-state ¹³C NMR experiments were carried out using a 500 MHz Varian spectrometer at ¹³C and ¹H frequencies (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.

Results and Discussions

The dark colour intensity of the filtered, measured by UV-Vis spectroscopy, showed a linear relationship with the NaOCl concentration (data not showed), indicating that the oxidant excess is still not reached.

The ¹³C NMR spectra of the obtained products (Figure 1) are characterised by a featureless aryl peak in the region of 130 ppm and a carboxyl peak at 169 ppm. This up field shift (smaller chemical shift value than regular carboxyl groups ~ 175 ppm) indicates carboxyl groups attached directly to the aromatic backbone.

The aryl peak of humic acids presented a smaller chemical shift value (128 ppm) than the one of fulvic acids (132 ppm), indicating that the former presents a more polycondensed aromatic structure. On the other hand, the fulvic acids presented a higher content of carboxyl groups than the humic acids.

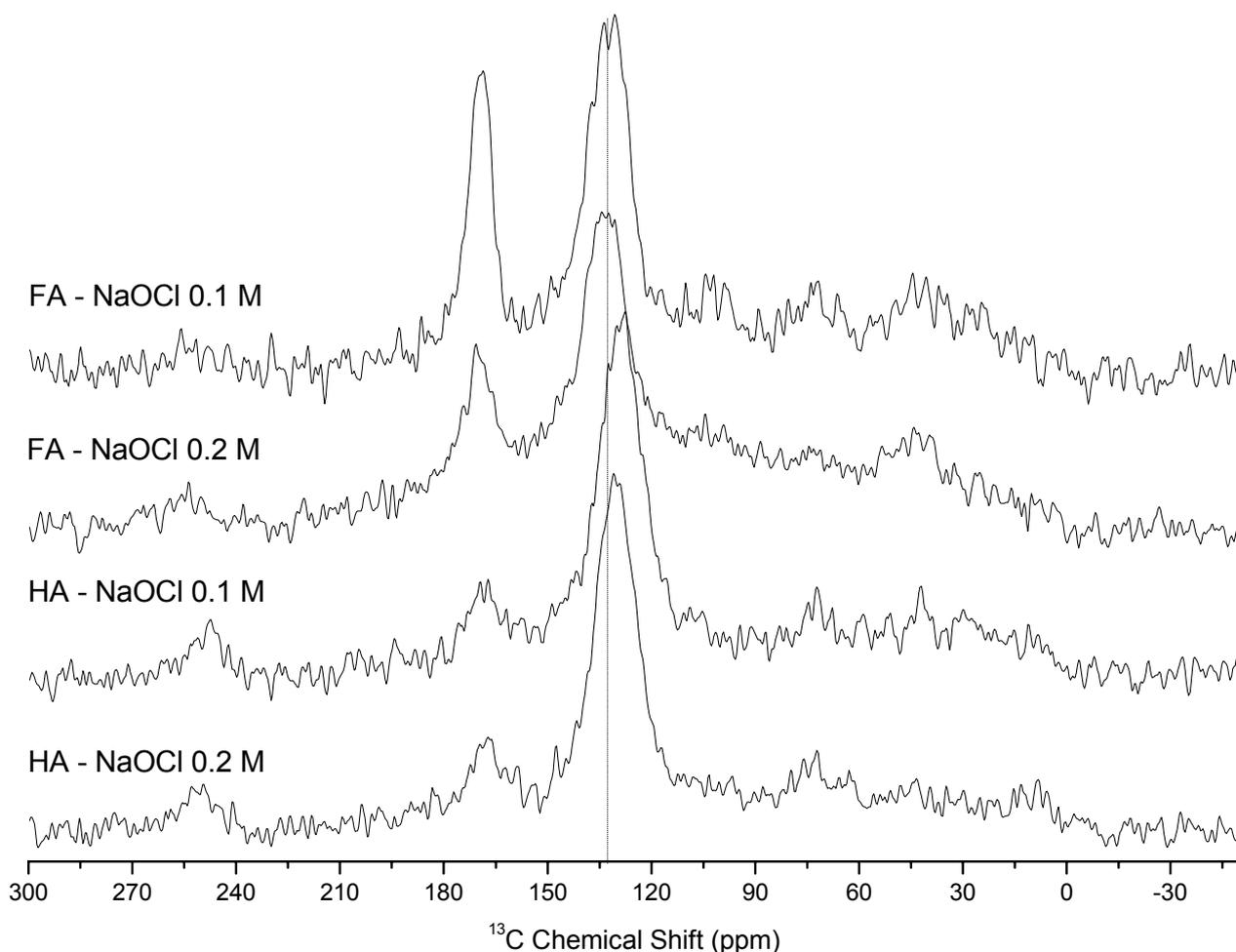


Figure 1. Solid State ¹³C NMR of the obtained products. FA – Fulvic Acids; HA – Humic Acids.

Conclusions

According to the obtained results, the functionalisation was effective, producing the expected compounds. The reaction yield was proportional to the oxidant agent concentration, indicating that the oxidant excess is still not reached. The fulvic acids were soluble at any pH value probably due to higher concentration of carboxylic moieties and also due to its lower aromatic ring condensation.

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[†] 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.