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Nanoscale Structure Of Organic Matter Explain Its Recalcitrance To Degradation

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Recalcitrance can be defined as the natural resistance of organic matter (OM) to microbial and enzymatic deconstruction (Himmel et al., 2007).
The nature of OM recalcitrance remained not completely understood and more studies need above all to elucidate the role of the chemical topography of the OM at nanometer scale.
Hydrolytic enzymes responsible of OM degradation have a molecular weight of 20-25 kD, corresponding to a size of about 4 nm, hardly penetrate into micropores (i.e. the pore having a diameter < 2 nm) and small mesopores (i.e. pores having a diameter 2 < 50 nm) of OM structures, so that their activities are confined only to a portion of the total surface (Zimmerman et al., 2004; Chesson, 1997; Adani et al., 2006). As consequence of that the characterization of the organic matter at nano-scale became interesting in view to explain OM recalcitrance.
The aim of this work was to asses the effect of the nano-scale structure of OM versus its recalcitrance.
The evolution of organic matter of organic matrices was studied in two systems: plant residue-soil system and simulated landfill system. Plant residues were incubated in soil for one year and recalcitrant fraction, i.e. humic acid, was isolated and studied. Laboratory simulated landfill considered organic fraction of municipal solid waste sampled at different stages of evolution from a full scale plant and incubated under anaerobic condition for one year.
In addition the nano-scale structure of fossilized OM (leonardite, chair coal and graphite) was detected as used as model of recalcitrant OM.
Nano-scale structures were detected by using meso and microporosity detection. In particular microporosity was determined by adsorption method using CO2 at 273 K and Non Local Density Functional Theory (NLDFT) method was applied to measure the CO2 adsorption isotherms. On the other hand mesoporosity was detected by using N2 adsorption method at 77 K. The BET (Brunauer-Emmett-Teller) equation and the BJH (Barret-Joyner-Halenda) equation were applied respectively to measure specific surface area and mesoporosity.
Macromolecular composition of OM was investigated by using CP MAS 13NMR and wet chemical analyses.
Results obtained showed how OM evolved increasing microporosity and decreasing meso porosity. This was the result of the preservation of recalcitrant OM versus degradation of the more labile fraction, suggesting that the more recalcitrant fraction was characterized by high microporosity. Another confirmation of these results comes from the analysis of the same OM after the removing of the labile fraction by acid hydrolysis to discover the core-OM, which was characterized by a higher microposrosity with respect the bulk OM.
In conclusion it can be showed that not only the chemical composition but, also, the physical structure of organic matter defined its recalcitrance.

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