Design of humic-based iron nanofertilizers: iron (hydr)oxide chemistry, nanoscale benefits, and multilevel impact of humic substances

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Iron deficiency, also known as chlorosis disease, is a frequent issue for numerous crops and strongly impacts agriculture in the countries rich in calcareous soils. This is due to the low availability of microscale iron(III) (hydr)oxides abundant in soils with pH > 7. Typical treatment of lime-induced chlorosis is the application of synthetic iron chelates such as Fe-EDTA, Fe–DTPA, Fe–EDDHA, etc. While these compounds rapidly provide plants with bioavailable iron, chelating agents can accumulate in soils, contaminate groundwater, and increase the mobility of heavy metals and radionuclides. The high cost is another important drawback of the iron chelate preparations. At the same time, nanosized (<5-20 nm) iron (hydr)oxides exhibit good availability to plants and within the recent decades became a versatile platform for the design of advanced iron nanofertilizers (Fe-NF). Because of high affinity to the iron oxide surface and rich beneficial effects on plants, humic substances (natural eco-friendly polyelectrolytes) are considered as the best stabilizing agent for Fe-NF. However, for mass production and effective utilization of the nanofertilizers, several fundamental and technological issues still should be solved, including identification of the most bioavailable iron (hydr)oxide nanoparticles (in terms of both phase composition and size), long-term stabilization of hybrid iron-humic colloids, and development of the most effective application routes considering the nanoparticle uptake and translocation in the target plants.

In the present conference contribution, we will discuss the most important features of Fe-NF production based on the extensive studies pursued by our group. We comprehensively characterize iron (hydr)oxide nanoparticles – the main part of the nanofertilizers – using state-of-the-art materials science techniques: analytical transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), extended X-ray absorption fine structure spectroscopy (EXAFS), and small-angle X-ray scattering (SAXS). We also use a great gift coming directly from the nuclei of Fe atoms: the ability to analyze iron speciation by Mössbauer spectroscopy including analysis of the frozen aqueous reaction mixtures and ^{57}Fe-enriched samples. These techniques allowed a deep understanding of nanoparticulate iron (hydr)oxide chemistry and important iron-humic interactions. Our bioassays include root application of Fe-NF to cucumber, wheat, and soybean plants grown in Hoagland / Knop nutrient solutions or model calcareous soil. Content of iron and chlorophyll *a* in the fertilized crops and their photosynthetic activity were monitored. Mass spectrometry chemical analysis of soybean shoots, pods, and roots fertilized with ^{57}Fe-enriched preparations was used as well to track Fe-NF translocation. Recent results on foliar spray application of the nanofertilizers would also be discussed.

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