

## Stabilizing ability of humic acids towards Fe<sub>3</sub>O<sub>4</sub> nanoparticles under various oxidation conditions

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Humic acids (HA), natural polyelectrolytes and strong chelates can effectively prevent the aggregation of magnetite nanoparticles, from one side, and from another side, HA as antioxidants can affect the iron species state. The increasing application of iron-based nanoparticles has raised concerns regarding their environmental behavior and potential ecological effects. After release into the environment, iron-based NPs undergo various transformations via the interactions with different geochemical and biological components, which ultimately influence their behavior and potential toxicity. In this study, the oxidation of HA-coated magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>-HA NPs) is investigated under mild and harsh conditions in order to understand the oxidation behavior and the chemical stability of transition forms in the presence of humic acids. XRD analysis and Mössbauer spectroscopy were used to identify the phase composition of NPs and the change in the oxygen environment of iron atoms.

The chemical precipitation *in situ* method with in the HA matrix or the self-assembly method was used to formulate the Fe<sub>3</sub>O<sub>4</sub> NPs from Fe(II) and Fe(III) salts by NH<sub>4</sub>OH addition in argon atmosphere. To simulate the oxidation process of the Fe<sub>3</sub>O<sub>4</sub>-HA three treatment ways were used: mild (storage in tap water during 24 hours, st) and two huge conditions (influence of concentrated HNO<sub>3</sub> or mechanical treatment in the grinder at 1400 rpm in 10 min in air atmosphere, mill). As a total, the following samples were analyzed: Fe<sub>3</sub>O<sub>4</sub>-HA (ini), Fe<sub>3</sub>O<sub>4</sub>-HA (st), Fe<sub>3</sub>O<sub>4</sub>-HA (HNO<sub>3</sub>) and Fe<sub>3</sub>O<sub>4</sub>-HA (mill) and NPs of Fe<sub>3</sub>O<sub>4</sub> (ini), Fe<sub>3</sub>O<sub>4</sub> (HNO<sub>3</sub>) as a control.

According to the XRD data, main phase for all samples tested before and after oxidation is a magnetite Fe<sub>3</sub>O<sub>4</sub> NPs. Complete phase transformation to maghemite Fe<sub>2</sub>O<sub>3</sub> for all samples under treatment (storage in H<sub>2</sub>O, nitric acid and mechanical treatment) was evidenced by Mössbauer spectroscopic measurements. Thus, XRD technique suffers from serious limitations and ineffective in discriminating magnetite. The oxidative degradation of Fe<sub>3</sub>O<sub>4</sub> to Fe<sub>2</sub>O<sub>3</sub> nanoparticles changed in the order: Fe<sub>3</sub>O<sub>4</sub> (HNO<sub>3</sub>) < Fe<sub>3</sub>O<sub>4</sub>-HA (st) < Fe<sub>3</sub>O<sub>4</sub>-HA (HNO<sub>3</sub>) < Fe<sub>3</sub>O<sub>4</sub>-HA (mill), and indicates oxidative effect of HA towards Fe<sup>2+</sup> ions.

Mitigating effect of HA on bioactivity of two types of iron oxide nanoparticles of Fe<sub>3</sub>O<sub>4</sub> and γ-Fe<sub>2</sub>O<sub>3</sub> to the green algae *Scenedesmus quadricauda* and the higher plant (seeds of white mustard *Sinapis alba*) a higher plant (white mustard) were investigated with a focus on the effect of oxidation state. Results show that the growth inhibition by iron oxides nanoparticles (NPs) to both test-species increased with oxidation of the NPs with an order Fe<sub>3</sub>O<sub>4</sub> (ini) < Fe<sub>3</sub>O<sub>4</sub>-HA (ini) < Fe<sub>2</sub>O<sub>3</sub>-HA (above Fe<sub>3</sub>O<sub>4</sub>-HA (mill)). The main toxic mechanism, which could explain the difference in toxicity of the NPs is probably Fe<sup>2+</sup> and Fe<sup>3+</sup> ions release. These findings will be helpful for the understanding of HA role on the fate and toxicity of iron-based NPs in the environment.

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