

Humic acids impact on bioactivity and aging of iron ions or nanoparticles

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At present the question still remains whether the toxicity of iron oxide nanoparticles (NPs) from the released ions or NPs itself arises and how humic acids (HA) can influence on toxicity of NPs. In this study effect of humic acids, a natural organic polyligand that easily coordinate to iron (II, III) ions and graft to Fe₃O₄ NPs surfaces, on behavior of Fe₃O₄-NPs were investigated in the aspects of their toxicity using standard test systems with higher plants *Sinapis alba* and invertebrates *Paramecium caudatum*. The Fe(II, III)-humic complexes were prepared by reaction of weighed amounts of the HA and the iron source with HA:Fe ratio of 1:0.150 (w/w). Colloidal Fe₃O₄-NPs were synthesized by a chemical precipitation method *in situ* when the magnetic particles are grown within the HA matrix that provides steric stabilization of the colloidal system.

Several treatments of the test cultures were made: a) control A – tap water without Fe and HA; b) control B – tap water with Fe (II) or/and Fe(III), c) control C – tap water with HA, d) five treatments with the following substances: Fe(II, III)-HA: Fe(II)-HA, Fe(III)-HA, Fe(II, III)-HA, Fe₃O₄-NPs and Fe₃O₄-NPs-HA. Endpoints (EC50) and threshold level (EC20) for samples with acute toxicity have been studied in test systems with *S. alba* and *P. caudatum*. The toxicity of the samples was also measured three months after storage. According to toxicity decreasing for both test cultures the studied samples can be arranged in the following order: Fe(II), Fe(II, III) ≥ Fe(III) > HA > Fe₃O₄-NPs-HA > Fe(III)-HA > Fe(II)-HA ≥ Fe(II, III)-HA >>> Fe₃O₄-NPs.

For higher plants *S. alba*, the addition of HA to Fe(II) and Fe(III) and their mixtures reduces their toxicity. However, when HA were added to Fe₃O₄-NPs, the toxicity of NPs increases significantly. In relation to infusoria *P. caudatum*, the addition of humic acids to Fe(II) ions and Fe(II, III) reduces their toxicity (in relation to the mixture - significantly). However, in the case of Fe (III) the toxicity of the complex increases after the addition of HA. The toxicity of the nanocomposite Fe₃O₄-NPs-HA decreases slightly compared to nanoparticles Fe₃O₄-NPs.

Three months after storage, the toxicity of humic acids and the composite Fe₃O₄-NPs-HA decreased in relation to higher plants *S. alba*. In relation to infusoria *P. caudatum*, complexes with HA also remained less toxic than ions Fe (II), Fe(III) and a Fe(II, III) of ions. However, the composite Fe₃O₄-NPs-HA turned out to be more toxic than HA and nanoparticles Fe₃O₄-NPs and this nanocomposite before storage.

Thus, the addition of humic acids reduces the toxicity of iron ions but increases the toxicity of Fe₃O₄ nanoparticles. After three months of storage humic acids become less toxic, however, nanocomposites Fe₃O₄-NPs-HA retain their toxic effect.

Interpreting the results was performed by a two-way ANOVA with interactions using XLSTAT Software, 2014. The treatment method (single HA, single NPs or their mixture) and the treatment concentration have a significant effect on acute toxicity samples. For both Fe₃O₄-NPs and Fe₃O₄-NPs-HA the toxicity more largely depend on the treatment concentration.

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