

The effect of humic acids adsorption on pH-dependent surface charging and aggregation of Fe₃O₄-APTES nanoparticles

Bondarenko L.¹, Illes I.², Tombácz E.², Magomedov I.¹, Rabinskiy L.¹, Kydraliev K.¹

¹Moscow Aviation Institute, Moscow, Russia, l.s.bondarenko92@gmail.com

²University of Szeged, Szeged, Hungary

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Humic acids (HA) are often used as a stabilizer for magnetite nanoparticles (Fe₃O₄) and as a functional component for magnetic nanocomposites. Despite the protective shell of HA the oxidative degradation of Fe₃O₄ to maghemite Fe₂O₃ nanoparticles is observed. This led to a change in the biological activity of the composite (*Terekhova et al., 2018*). To improve chemical stability of Fe₃O₄ the surface charge control was used through pre-treatment using silanes. In this study, effect of HA adsorption on pH-dependent surface charging and aggregation of the Fe₃O₄ functionalized by 3-aminopropyl-triethoxysilane (APTES) was studied. A set of the Fe₃O₄-APTES samples were formulated: under argon (Ar) or air atmosphere and/or further dialysis (D) and subsequent treatment of the samples: in harsh (US-treatment) and mild (magnetic stirrer, M) conditions. As a total, five samples were obtained: Fe₃O₄, Fe₃O₄-APTES (Ar), Fe₃O₄-APTES (Ar-D-M), Fe₃O₄-APTES (Ar-D-US), and Fe₃O₄-APTES (air).

Magnitude of isoelectric points (iep, the pH of $\xi = 0$), zeta-potential and hydrodynamic size were measured at 25 ± 0.1 °C in a disposable zeta cell (DTS 1060) of NanoZS (Malvern, UK) apparatus [2]. The range of pH was between ~3 and ~10. According to the magnitude of the shift of the pH-dependent zeta potential functions due to the sorption of increasing amount of HA in case of all samples, it is possible to formulate a series of samples in which the sorption capacity decreases: Fe₃O₄-APTES (Ar-D-M) ≥ Fe₃O₄-APTES (air) > Fe₃O₄ ≥ Fe₃O₄-APTES (Ar-D-US) >> Fe₃O₄-APTES (Ar).

Treatment way has a great effect on the sorption capacity of the samples. Dialysis of the sample Fe₃O₄-APTES (Ar) led to enhance adsorbing of HA. The sample exposed to the magnetic stirrer has a larger sorption capacity than the sample after the US-treatment: Fe₃O₄-APTES (Ar-D-M) > Fe₃O₄-APTES (Ar-D-US) >> Fe₃O₄-APTES (Ar). It is likely that harsh conditions during sonication (extreme high temperature and pressure in cavities forming at interfaces) led to destroy Fe₃O₄-APTES-HA bonds and reduce the sorption capacity.

The hydrodynamic diameter increases near the isoelectric point for the samples Fe₃O₄-APTES without HA. The hydrodynamic size for the samples Fe₃O₄-APTES at pH < 5 and pH > 9 varied from 700 nm to 300 nm. In the range 5 < pH < 9, the hydrodynamic size is about 100-300 nm. But, the hydrodynamic diameter for Fe₃O₄-APTES the increases near the isoelectric point (from 200 to 750 nm), when not fully coverage with HA. In case of full coverage with HA, the hydrodynamic size remains unchanged at all pH range (around 150 nm for all of samples).

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References

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