Stabilization of Iron Oxide Magnetic Nanoparticles with Different Morphology in Aqueous Suspensions Using Humic Substances

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1. Introduction

A use of magnetic liquids for therapy of cancer diseases is an important branch of modern biomedical technologies. The magnetic nanoparticles suitable for those applications should be biocompatible and stable in aqueous suspension. Ferric oxides represent one of the most biocompatible magnetic phases which forms a variety of different morphologies.

Humic acids (HA) are a complex mixture of natural macromolecular compounds with vast functional periphery dominated by carboxyl and hydroxyl groups. They possess polyelectrolite properties and distinct surface activity. Thereupon, they can bind nanoparticles both by electrostatic surface interactions and by complex formation [1]. Humic acids were reported to be suitable stabilization agents for magnetite (Fe_3O_4) suspensions [2]. However Fe_3O_4 could be oxidized to Fe^{III}-compounds in physiological medium and this can lead to adverse consequences. At the same time δ-FeOOH and γ-Fe_2O_3 do not have such shortcomings and possess necessary magnetic properties.

Thereupon, the objective of this work was to synthesize feroxyhyte (δ-FeOOH) and maghemite (γ-Fe_2O_3) nanoparticles and to study the stability of their suspension in the presence of HAs.

2. Materials and Methods

Synthesis and characterization of iron oxide nanoparticles. Nanoparticles of δ-FeOOH and γ-FeOOH were synthesized by oxidation of "green rust" under different conditions. Nanoparticles of γ-Fe_2O_3 were obtained by annealing of γ-FeOOH at 200-250^{o}C. Phase composition of obtained nanoparticles was proven by X-ray phase analysis (Rigaku D/Max-2500 diffractometer). Morphology of the nanoparticles was characterized by using Hitachi H-8100 transmission electron microscope (TEM). Magnetic properties of synthesized compounds were studied by using Faraday balance magnetometer.

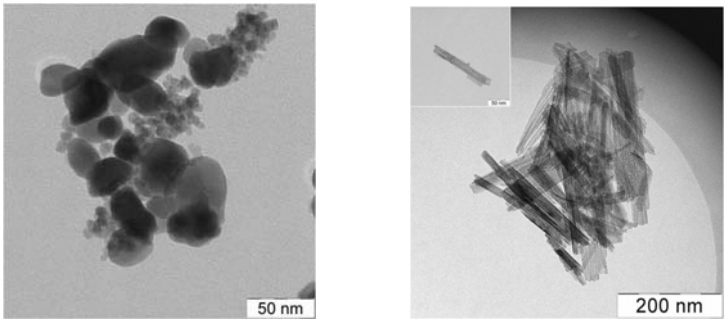
Preparation of humic materials and suspensions. Humic materials used in this work were HAs isolated from leonardite. The HA were dissolved in 1M NaOH under ultrasonic treatment. Then the solution was diluted with distilled water and pH was set to 7.00–7.05. Magnetic nanoparticles were added directly into HA solutions with subsequent ultrasonic treatment. Suspensions were kept at 4–5^{o}C and their stability was monitored. Suspensions of the nanoparticles in distilled water were used as blank experiments.

Iron (III) concentration in supernatant was monitored as main parameter of suspensions stability. Sample preparation was carried out according to conventional thiocyanate technique [3]. Optical density were measured by Varian Cary 50 Probe spectrophotometer at λ = 480 nm.

Size of colloidal particles and salt tolerance of suspensions were tested by using Zetasizer (Malvern, UK) apparatus based on dynamic light scattering (DLS).

3. Results and Discussion

Synthesis of magnetic nanoparticles. Two different morphologies were investigated in this work. We have synthesized δ-FeOOH nanospheres (average diameter ~ 30–40 nm, associated into 200 nm aggregates) and γ-Fe_2O_3 nanorods (~ 200–250 nm length, ~ 10–15 nm width) (Fig. 1).



a) *b)*

Figure 1: TEM images of δ-FeOOH – a) and γ-Fe_2O_3 – b)

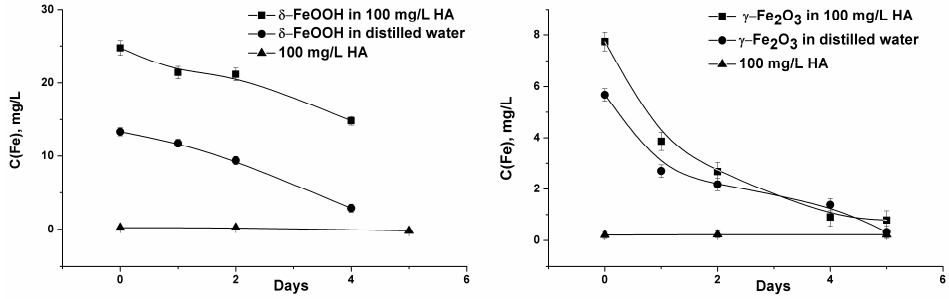
Nanoparticles of both iron oxides synthesized in this work were monophase as determined by X-ray phase analysis. Monophase δ-FeOOH has lattice parameters *a*=2.956(2); *c*=4.519(3) and monophase γ-Fe_2O_3 has lattice parameter *a*=8.3395(3).

Magnetic measurements show that both δ-FeOOH and γ-Fe_2O_3 display ferromagnetic properties. Feroxyhyte δ-FeOOH has saturation magnetization (M_s) ~ 18 emu/g and coercive force H_c = 110 Oe. Maghemite γ-Fe_2O_3 has M_s = 45 emu/g and H_c = 182 Oe. At the same time magnetite (Fe_3O_4), which often is synthesized for hyperthermia experiments, has

saturation magnetization up to 190 emu/g and coercive force from 32 to 65.5 Oe [4]. Thus, the synthesized nanoparticles possess magnetic properties comparable to those of magnetite and are suitable for biomedical application.

Study of magnetic suspensions stability in water. During storage magnetic suspensions gradually coagulate and large colloid particles precipitate. Thereupon, stability of the prepared suspensions was characterized by measurements of iron (III) concentration and colloidal particles size in supernatant.

The stabilisation of the obtained nanoparticles with HAs was studied in the broad range of concentrations. It was shown that the concentration of 100 mg/L of HA in solution provides the best conditions for stabilization of synthesized magnetic phases. At this concentration, up to 14.7 mg/L of iron (III) in the form of feroxyhyte nanoparticles were still stabilized after 4 days of observation (Fig. 2a). At the same time stabilization of maghemite nanoparticles was much worse (Fig. 2b). The difference between two oxides could be explained by the presence of large amount of hydroxyl groups on surface of feroxyhyte nanoparticles, whereas hydroxyl groups on maghemite surface are lost during annealing. In addition, γ-Fe_2O_3 nanoparticles have rather big size and shape anisotropy. Thus, morphology of magnetic nanoparticles and presence of surface hydroxyl groups have a significant impact on stability of suspensions.



a) *b)*

Figure 2: Content of stabilized iron in presence of HA: a) – δ-FeOOH nanospheres, b) – γ-Fe_2O_3 nanorods.

The DLS data show that nanoparticles quickly aggregate in suspensions without HA, whereas the presence of HAs sustains initial size of dispersed nanoparticles. Of particular importance is that the size of humic colloids without and with iron oxide nanoparticles does not differ significantly. This allows for suggestion that magnetic nanoparticles are captured into branched structure of HAs which play a role of "nanocontainer" (Fig. 3).

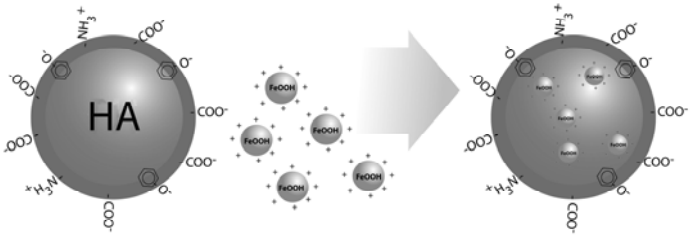


Figure 3:Supposed mechanism of stabilization of magnetic nanoparticles suspensions by HA

Magnetic suspensions for biomedical applications must be stable in physiological salt solution, whereas ionic strength has a significant impact on stability of suspensions [2]. Thereupon, we have characterized salt tolerance of the prepared magnetic suspensions by coagulation kinetic measurements in the presence of different concentrations of NaCl. Suspensions stabilized by HAs are stable in presence of 150 mmol/L NaCl (concentration of physiological salt solution); whereas suspensions of magnetic nanoparticles in distilled water possess very low salt tolerance (~ 30 mmol/L NaCl).

4. Conclusions

Characterization of magnetic suspensions stability displays that HAs are suitable stabilization agent for iron oxide nanoparticles particularly for feroxyhyte (δ-FeOOH) and maghemite (γ-Fe_2O_3). Measurements of iron (III) concentration in supernatant of suspensions show that feroxyhyte isotropic (spheroidal) nanoparticles with large amount of hydroxyl groups at their surface are stabilized much better than anisotropic annealed maghemite nanorods. According to salt tolerance measurements magnetic suspensions stabilized by HAs are stable in physiological salt solution. These results show a good promise for development of new biologically active magnetic preparations based on ferric-humic interactions.

References

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