Magnetic activity of nanostructured biopolymeric nanomagnets

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The magnetic properties of arabinogalactan-stabilized iron-containing nanobiocomposites, which include magnetite nanoparticles, were studied. The magnetic characteristics of samples were measured on a SQUID magnetometer in the temperature range of 5—320 K and magnetic fields of up to $1.5 \cdot 10^4$ G. The coercive force and the residual magnetization of ferroarabinogalactan nanocomposites are inversely dependent on the magnetite nanoparticle size.

Key words: iron oxides, magnetite, biopolymers, arabinogalactan, nanoparticles, nanobiomagnet.

Nanodispersed magnetic materials, which are polymer-coated magnetic nanoparticles, have attracted considerable attention.[1—9] In recent years, various aspects of nanosized magnetic materials, including magnetic metal oxide nanoparticles, such as their chemical synthesis, investigations of the structures, and the characterization of the magnetism, have been summarized and discussed in reviews and monographs.[1,2,10,11] The magnetism of nanoparticles is determined by their size, the shape of the surface, and interactions between the particles.[1] Iron oxides, particularly, magnetite, maghemite, hematite, and transition metal ferrites, are most often used as magnetic phases.[1—3,10,11] The biomedical application of nanomaterials was demonstrated by an example of nanosized iron oxides.[12—15] The successful use of magnetic iron oxide nanoparticles for the bio-drug delivery or the visualization of the features of biological materials at the cell or even molecular level confirms the importance of these studies.

Classical hydrolytic methods are the simplest and easy-to-implement methods for the synthesis of iron oxide particles, the co-precipitation method being most widely used.[10,14] The latter method is very simple, but its drawback is that the particle growth cannot be inhibited when the particle size exceeds the nanosized level. To prevent the excess growth of particles, various compounds consisting of both polymer and small molecules are used as stabilizing agents.[1,3] Inorganic iron oxide particles and the same particles encapsulated into an organic matrix, which were synthesized in a similar way, differ primarily in the size and, correspondingly, properties. The physical and chemical, as well as biological, properties of iron oxide particles having different sizes vary depending on the employed particle coating agent.[3,12—15]

A distinguishing feature of the classical hydrolytic method developed in our investigations is that the nanomagnets synthesized according to this method are characterized by good biocompatibility, the narrow particle dispersion distribution, and the homogeneous phase composition. The aim of the present study was to design nanostructured nanobiomagnets and to reveal the relationship between the composition and the magnetic parameters of the resulting nanocomposites.

Experimental

The following reagents were used: $FeSO_4 \cdot 7H_2O$ (reagent grade), $FeCl_3 \cdot 6H_2O$ (reagent grade), ammonium hydroxide (special purity grade), and EtOH (reagent grade). Arabinogalactan was isolated from an aqueous extract of larch wood and purified by percolation through a polyamide sorbent followed by the reprecipitation with EtOH.

Nanobiocomposites of ferroarabinogalactans were synthesized according to a procedure described previously.[16] An aqueous solution (2 mL) containing $FeSO_4 \cdot 7H_2O$ (0.029—0.245 g) and $FeCl_3 \cdot 6H_2O$ (0.055—0.477 g) in a molar ratio of 1 : 2 was added with vigorous stirring to a solution of arabinogalactan (1 g) in water (2 mL), and the reaction mixture was kept at 300 K for 30 min. Then a 30% aqueous ammonium hydroxide solution was added to pH 10—11. The solution was heated on a boiling water bath for 15 min and filtered through a paper filter. The target products were isolated from the filtrate, purified from admixture of low-molecular-weight components by double reprecipitation with ethanol, and dried *in vacuo*. The iron content in the nanocomposites determined by atomic absorption spectro-

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scopy was 3.5—16.3%. The yields of the target products were 85.7—96.8%.

Micrographs of metal-containing nanoparticles were taken with a Leo 906E transmission electron microscope at an accelerating voltage of 80 kV. The particle size and the particle size distribution were determined by the statistical processing of the electron micrographs.

The magnetic properties of ferroarabinogalactans were measured on an MPMSXL SQUID magnetometer in the temperature range of 5—320 K and magnetic fields of up to $1.5 \cdot 10^4$ G.

Results and Discussion

We studied the magnetic activity of the new in principle type of nanobiomagnets, which are aggregation-stable nanodispersed magnetite samples encapsulated into a biopolymer matrix.[16,17] The polysaccharide arabinogalactan was used as the matrix providing the self-organization of the system, resulting in the self-assembly of nanoparticles to form ordered nanosized inorganic-organic hybrid nanocomposites. Due to the use of the natural polysaccharide with hydrotropic properties as the stabilizing agent, the products are water-soluble. In the course of the experiment, it was found that to maintain the system in the aggregatively stable state, it is necessary that the metal salt-to-polysaccharide ratio should be 0.1—2.2 mmol g^{-1} and the medium, in which the co-precipitation and formation of iron oxide occur, should be alkaline. Under these conditions, a series of nanobiocomposites (ferroarabinogalactans) with a total iron content varying from 3.5 to 16.3% and the controlled dispersion of iron oxide nanoparticles were prepared.

It is known[3,10] that the magnetic characteristics of nanoparticles can be, to a certain extent, changed by varying their morphology in the composite (the size, the shape, the composition, the core-to-shell ratio, and the arrangement of particles in the matrix). The most suitable and simple way to influence the magnetic parameters of nanocomposites is based on changes in the quantitative magnetic core-to-polymeric organic shell ratio. Due to the possibility of the control of the particle size by the dose addition of a metal-containing precursor to the solution, the resulting magnetite particles have the specified narrow size distribution. The structures of nanocomposites containing highly dispersed magnetite Fe_3O_4 (see Ref. 18) were determined by powder X-ray diffraction and scanning transmission electron microscopy. The size of the resulting magnetite nanoparticles varies (from 4 to 10 nm) depending on the total iron content in the nanocomposites (Fig. 1); the particles are spatially separated by the organic matrix at distances equal to, or larger than, their diameter. The particle size distributions in all nanocomposites are unimodal and narrow. For example, the fraction of particles with a size of 3—5 nm in the sample containing 3.5% of iron is 74% (Fig. 2). An increase in the iron content in the samples by a factor of more than four leads to an increase in the size of magnetite particles by a factor of approximately two (Fig. 3).

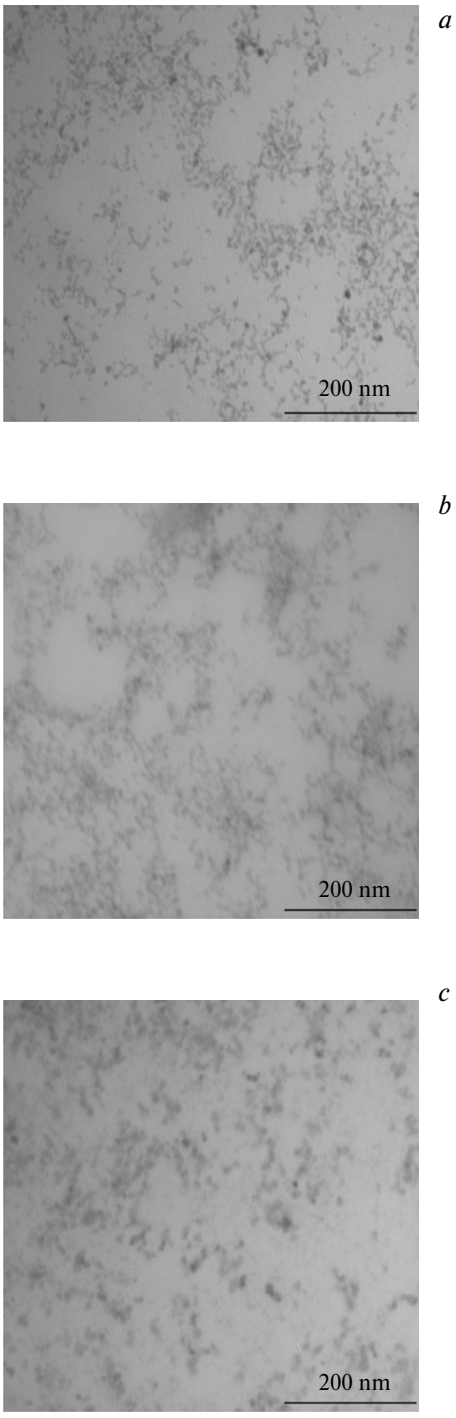

Fig. 1. Transmission electron microscopy images of magnetite nanoparticles in the nanomagnet ferroarabinogalactan containing 3.5 (*a*), 8.1 (*b*), and 16.3% of iron (*c*).

The magnetic properties of nanostructures are diverse and substantially differ from those of the bulk material.[1,10] The presence of nanosized magnetite in ferroarabinoga-

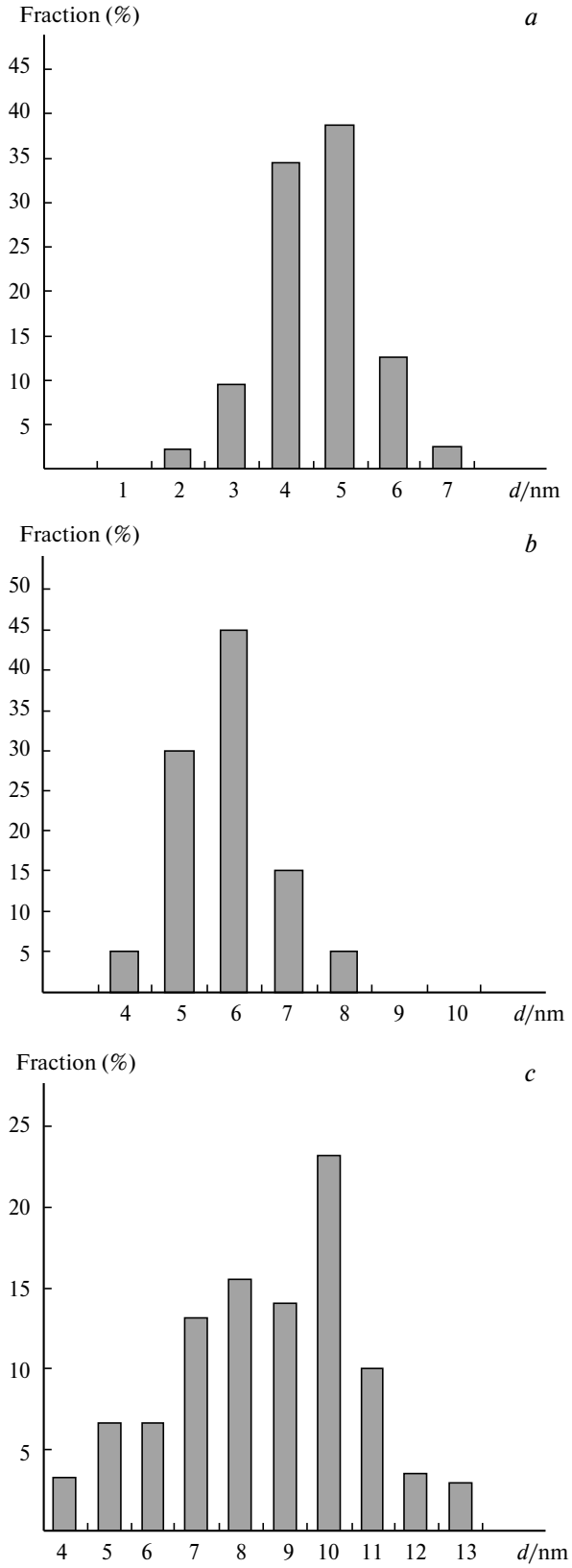

Fig. 2. Size distribution of magnetite nanoparticles (d) in the nanomagnet ferroarabinogalactan containing 3.5 (*a*), 8.1 (*b*), and 16.3% (*c*) of iron.

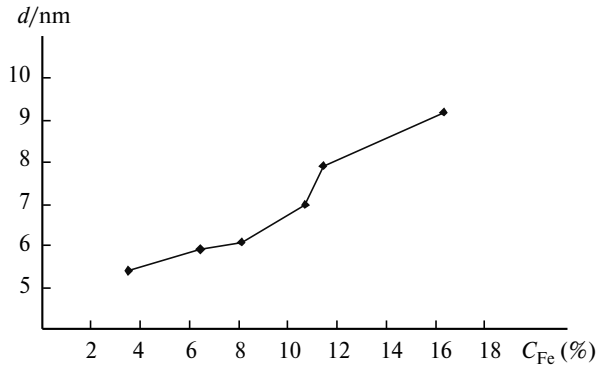

Fig. 3. Plot of the diameter (d) of the nanoparticles *versus* the iron content (C_{Fe}) in nanocomposites.

lactans is responsible for their specific magnetic characteristics.

The fundamental magnetic properties of ferroarabinogalactans containing different amounts of ferromagnetic iron in the form of magnetite nanoparticles Fe_3O_4 were measured in magnetic fields up to $1.5 \cdot 10^4$ G. The curves of the magnetization (σ) were recorded both in the low-temperature range (5 K) and at 320 K. The plots of the magnetization *versus* the external magnetic field strength measured duing alternating magnetization of the ferroarabinogalactans under study show a hysteresis loop (Fig. 4). The residual magnetization (σ_{res}) and the coercive force (H_c) are the main characteristics of the hysteresis loop. In the case under consideration, these characteristics depend on both the iron content in the composites and the temperature of measurements.

The residual magnetization measured in the low-temperature range (5 K) decreases from 43.8 to 21.0 G cm^3 g^{-1} with increasing iron content in nanocomposites (Table 1). The coercive force evaluated for nanomagnetites at 5 K

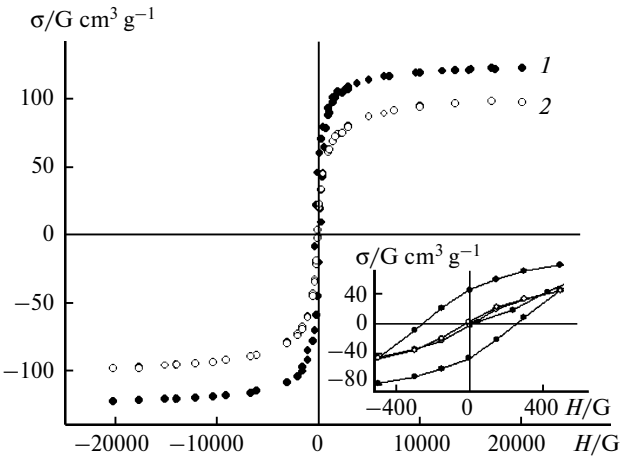

Fig. 4. Typical curves of the magnetization (σ) of the nanomagnet ferroarabinogalactan at 5 (*1*) and 320 K (*2*). The inset shows the magnified curves of the magnetization.

Table 1. Experimental values of the residual magnetization (σ_{res}) and coercive force (H_c) at 5 K and the specific magnetization (σ) at 5 and 320 K per unit weight of iron in the nanocomposite

Sample	C_{Fe} (%)	σ_{res} /G cm^3 g^{-1}	H_c /kA m^{-1}	σ/G cm^3 g^{-1}	
				5 K	320 K
1	3.5	43.8	20.45	122.7	97.4
2	6.4	35.2	18.94	104.0	78.6
3	8.1	35.8	19.34	107.0	84.3
4	10.7	34.2	17.75	101.0	79.0
5	11.4	28.0	17.03	87.7	66.4
6	16.3	21.0	18.30	67.0	47.2

decreases from 20.45 to 17.03 kA m^{-1} with increasing iron content and nanoparticle size (see Table 1). An increase in the temperature leads to a decrease in the coercive force because the thermal motion of atoms caused by the heating of magnetic materials disturbs the parallel orientation of the spin magnetic moments.[10] At 320 K, the hysteresis loops of all the samples under study have the smallest parameters. In this case, the area of the dynamic hysteresis loop decreases due to a decrease in the energy absorbed by the nanomagnet. Consequently, the temperature influences the magnetic properties of ferroarabinogalactans. Nevertheless, the compositions and the structures of nanomagnets with spatially separated magnetic particles are responsible for the retention of the magnetization even at 320 K, as opposed to most of materials of this type.[1] It was found that the specific magnetization of samples as a function of the magnetic field strength in the low-temperature range (5 K) decreases with increasing iron content in the samples. An increase in the temperature does not lead to changes in this dependence, but results in a gradual decrease in the σ value (Fig. 5).

In addition, the size effect on the change in the magnetic properties of the samples would be expected to appear due to the variable magnetite nanoparticle size.[14,19] As mentioned above, an increase in the magnetite particle size from 4 to 10 nm leads to a decrease in the specific and residual magnetizations. Consequently, the magnetization is inversely proportional to the size of iron-containing nanoparticles in nanocomposites.

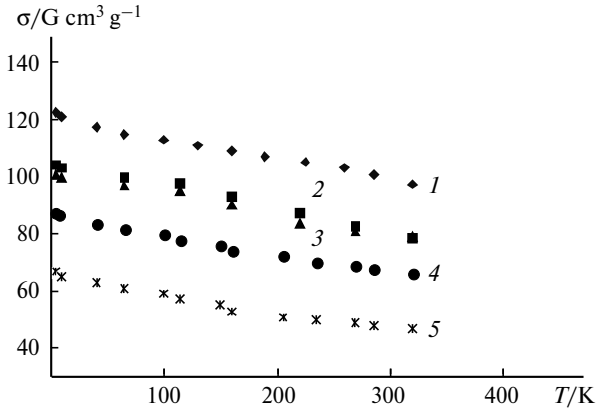

Fig. 5. Temperature dependences of the magnetization (σ) of nanocomposites containing 3.5 (*1*), 6.4 (*2*), 10.7 (*3*), 11.4 (*4*), and 16.3% (*5*) of iron.

To sum up, we designed nanomagnets with spatially separated magnetic agents and found that the composition and the structure of the resulting nanobiomagnets are related to the fundamental magnetic properties. It was shown that the specific and residual magnetizations of ferroarabinogalactan nanocomposites throughout the temperature range under study, as well as the coercive force in the low-temperature range, are inversely dependent on the magnetite nanoparticle size. These materials are of interest for the design of biocompatible multifunctional materials having technical and medical application (biocompatible magnets, magnetic liquids, magnetic contrast agents for tomography, and magnetically localized agents) with controlled magnetic properties.

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