Magnetite-polymer Nanoparticles: Structure and Properties

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The paper describes synthesis of magnetite-alginate composites. The main feature of such biomaterials is the simultaneous formation of magnetite nanoparticles inside the alginate matrix. Obtained samples were characterized by X-ray diffraction and transmission electron microscopy. In several samples the secondary phase of ammonium chloride was observed. The average crystallite sizes of magnetite phase are about 13 nm. The addition of alginate leads to the decrease of microstrains in [$h\,k\,0$] direction.

Keywords: Magnetite, Alginate, X-ray diffraction, Transmission electron microscopy.
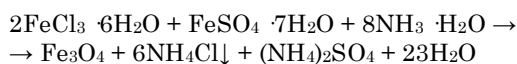
1. INTRODUCTION

Unique properties of magnetite nanoparticles are widely used in medicine for diagnostics and treatment. It is considered that biomagnetite is very important for preservation and processing of data in brains. It was shown that signals, caused by the physiogenic and pathogenic magnetic biominerals, are registered in brain tissues [1]. We have developed several ways to obtain magnetite granules in a polysaccharide shell for medical purposes [2]. For a detailed study of a role of magnetic biominerals in the brain function, it is necessary to develop biomimetic technologies of the creation of their synthetic counterparts close to the conditions of the biominerals formation in the living body.

This paper describes properties and the synthesis of magnetite-alginate composites obtained by the formation of the nanostructured magnetite in the simultaneously created alginate matrix.

2. MATERIALS AND METHODS

2.1 Materials

Compounds of bivalent ($FeSO_4 \cdot 7H_2O$) and trivalent ($FeCl_3 \cdot 6H_2O$) iron (produced by "Sigma"), sodium alginate with the molecular weight of 323 kD (made in China), 25 wt % aqueous solution of ammonia were used. The formation of magnetite Fe_3O_4 (reference Sample 1) occurred at 80 °C according to the following chemical reaction:

$$2FeCl_3 \cdot 6H_2O + FeSO_4 \cdot 7H_2O + 8NH_3 \cdot H_2O \rightarrow$$
$$\rightarrow Fe_3O_4 + 6NH_4Cl\downarrow + (NH_4)_2SO_4 + 23H_2O$$

Magnetite nanoparticles for Samples 2-6 were formed in the presence of the natural polymer of sodium alginate. Fe^{2+} ions were added on the first stage to 2 wt % aqueous solution of alginate to achieve the equal distribution of magnetite nanoparticles in the alginate matrix for Samples 2-4. We assume that due to the joining-up of iron ions and functional groups of alginate the three-dimensional polymeric matrix was formed. Fe^{2+} ions acted as the centers of the following creation of magnetite. Ammonia solution was added on the differ-

ent stages of synthesis at 40 to 80 °C.

The synthesis of Samples 5 and 6 was focused on obtaining magnetite nanoparticles as a part of the aqueous-alginate emulsion. At the same time the alginate solution was added whether on the last stage after magnetite formation involving ammonia (Sample 5), or before its formation (Sample 6).

2.2 Methods

The crystallinity and structure of the synthesized samples were examined using an X-ray diffractometer DRON-3 (Bourevestnik, Inc., Saint-Petersburg, Russian Federation) connected to a computer-aided system for the experiment control and data processing. The current and the voltage of the X-ray tube were 20 mA and 40 kV respectively. All experimental data was processed by means of the program package DIFWIN-1 (Etalon PTC, Ltd., Moscow, Russian Federation). Identification of crystal phases was done using a JCPDS card catalog (Joint Committee on Powder Diffraction Standards).

The crystallite sizes L were calculated using the Scherrer equation [3]:

$$L = \frac{K\lambda}{\beta \cos\theta}, \qquad (2.1)$$

where K is the form coefficient ($K = 1$), λ is the wavelength, β is the peak broadening, θ is the diffraction angle.

The quantitative phase analysis was performed using the reference intensity ratio (RIR) method [4]:

$$C_i = \left(\frac{K_i I_i^{rel}}{I_i} \sum_{i=1}^{n} \frac{I_i}{K_i I_i^{rel}} \right)^{-1}, \qquad (2.2)$$

where C_i is the concentration of the i-phase, K_i is the corundum number of the i-phase, I_i is the peak integral intensity of the i-phase, I_i^{rel} is the peak relative intensity of the *i*-phase.

Due to the presence of two lines, which correspond to parallel planes of the same reflection order, it is possible. The Williamson-Hall method [3] was used to sep-

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arate contributions in the peak broadening from small sizes of coherent scattering regions and existing microstrains due to the presence of two lines, which correspond to parallel planes of the same reflection order.

The extrapolation function method was used to calculate a crystal lattice parameter. This method allows to extrapolate the lattice parameter value to the $\theta = 90°$ where definition errors of interplanar spaces, as well as the lattice parameter, are extremely low. The Nelson-Riley extrapolation function was used in our studies [3].

Electron microscopic studies were conducted after the ultrasonic dispersion of the samples using the transmission electronic microscope PEM-125K (SELMI, PTC, Sumy, Ukraine) with the 90 kV accelerating voltage and the 100 μA beam current. The linear crystallite particle sizes of samples were measured with the VideoTesT-Razmer 5.0 program (VideoTesT, Ltd., Saint-Petersburg, Russian Federation).

3. RESULTS

The X-ray diffraction phase analysis shows that the main phase of all samples is magnetite (JCPDS 75-1609). In several samples, namely 2, 3, 4 and 6, the secondary phase of ammonium chloride (JCPDS 73-1491) is also present. X-ray diffraction spectra are presented on Fig. 1. The quantitative phase analysis was performed to determine phase concentrations. The

Sample 3 has the largest quantity of ammonium chloride, while the least one is in the Sample 6.

Fig. 1 – X-ray diffraction spectra of synthesized samples

The average crystallite sizes of magnetite phase by Scherrer of all samples are about 13 nm varying from 11 to 18 nm (see Table 1). Polymer-bearing samples show slightly larger crystallite sizes with the decrease of microstrains as compared to the Sample 1 synthesized without alginate. The lattice parameter of Fe_3O_4 changes insignificantly.

Table 1 – Appointment of special paragraph styles

Samples	L (Schrerrer), nm					C, %		Williamson-Hall		Nelson-Riley
	(2 2 0)	(3 1 1)	(4 0 0)	(5 1 1)	(4 4 0)	NH_4	Fe_3O_4	L, nm	$\varepsilon \cdot 10^3$	a, nm
1	12,7	11,3	11,9	10,5	9,8	–	–	18	3,435	0,8342
2	12,1	13	12,8	13,9	11,7	33,8	66,2	12,6	0,411	0,8372
3	–	12,5	–	–	10,3	60,4	39,6	–	–	0,8366
4	–	13	–	13,5	11,6	43,3	56,7	–	–	0,8362
5	–	13,1	–	–	11,3	–	–	–	–	0,8355
6	18	17,9	13,7	16,4	18,1	18,7	81,3	17,8	0,061	0,836

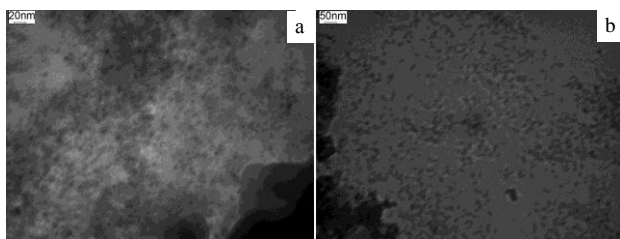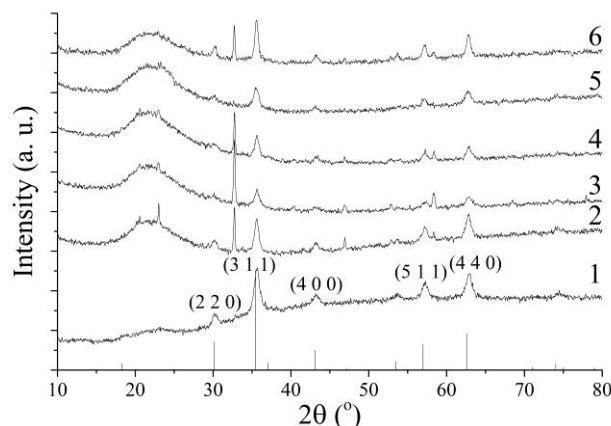TEM microphotographs show particles evenly distributed in an organic matrix (Fig. 2).

Fig. 2 – TEM microphotographs of magnetite nanoparticles, immobilized in alginate matrix: Samples 2 and 3 synthesized with different techniques

4. CONCLUSIONS

It was found that the formation of the unwanted phase of ammonium chloride in several samples depends on the temperature conditions of synthesis. The magnetite nanoparticles, evenly incorporated into the alginate matrix, with similar crystallite sizes were obtained during researches. The aim of our future development is to improve the synthesis techniques and to study structural properties of magnetite in biopolymer matrices.

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