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## Synthesis of a Magnetite Nanoparticle System for use in Drugs with Magnetic Properties

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**Abstract** Synthesis of magnetite particles was performed by chemical coprecipitation in alkaline medium (pH = 10-11) using the solutions of sodium hydroxide, potassium hydroxide and 25% ammonium hydroxide. The use of an excess solution of ammonium hydroxide allows obtaining a system of magnetite particles, the saturation magnetization of which exceeds almost three times this parameter for particles synthesized using alkali solutions. It was found that the synthesis should be carried out with the use of excess of 1.75 iron (II) salt in ammonium hydroxide at pH = 10-11.

It was proved (X-ray diffraction method) that the chosen method allows to obtain the particles of colloidal magnetite size  $\langle d \rangle = 16$  nm without impurities with the correct parameters of the crystal lattice with high magnetic properties that can be used to create drugs with magnetic properties.

**Keywords** Magnetite nanoparticle, magnetic fluid, coprecipitation method

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### Introduction

The creation of magnetic medicines with nanoparticles of magnetite (other ferrites) is a new promising scientific branch [1-8]. Pharmaceutical agent with magnetic properties solves targeted delivery of the active substance, fixation of the agent (using an external magnetic field) in the pathology area, localizing therapeutic dose, minimizes toxic-allergic reactions of the body, opens new methods of local treatment, the most optimal and rational [9-12].

The industrial production of magnetite is fairly well-tuned and multi-tonnage [13-15], but it is aimed at producing magnetite for technical applications with a minimum particle size of 1-2 microns. Smaller particles of magnetite are obtained by grinding or condensation — thermal, electrolytic, vacuum, chemical.

Chemical condensation method can produce magnetite of colloidal size, which has a minimum of easily removed impurities. In addition, it is quite simple, does not require expensive equipment and allows to obtain magnetite particles of several nanometers in size.

In experimental work, magnetite was obtained by the method of chemical condensation from aqueous solutions of salts of iron (II) and iron (III) in alkaline medium by the reaction equation:



In order to obtain magnetite particles with high functional properties, experimental studies were conducted to select the conditions for conducting the magnetite synthesis reaction.



## Materials and Methods

The synthesis was performed in alkaline medium (pH = 10-11) using the solutions of sodium hydroxide, potassium hydroxide and 25% ammonium hydroxide. The starting materials iron (III) chloride and iron (II) chloride were used in a stoichiometric ratio and using an excess of 1.75 times the salt of iron (II).

For all cases, the synthesis reaction was performed using a single algorithm. To a filtered 10% solution of iron (II) and (III) salts with slow stirring and temperature  $T = 50-60\text{ }^{\circ}\text{C}$  a small trickle excess hydroxide solution to create pH = 10-11 were added. The formation of a black precipitate immediately and the increasing of temperature to 7-8  $^{\circ}\text{C}$  were observed. In one hour, the heat is turned off and stirring is continued until the mixture is cooled. The reaction mixture is then kept in a constant magnetic field for 12 hours; thereafter, the solution is repeatedly washed by magnetic decantation to pH = 9÷10.

Iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 97%), iron (II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , 99%) were used (Merck, Germany). All other chemicals were of analytical reagent grade and were used without further purification. The synthesized magnetite particles were certified for their magnetic properties. The magnetization measurements were done at room temperature by using vibrating sample magnetometer (VSM). Magnetic hysteresis loops were experimentally determined for the synthesized magnetite samples ( $T = 300\text{K}$ ). The crystalline structure of magnetite nanoparticles were studied by means of X-ray diffraction (XRD). The X-ray diffraction pattern of the sample were recorded on a SiemensD500 X-ray powder diffractometer using copper radiation. The crystallite size of the sample was measured from the X-ray line broadening using the Debye-Scherrer formula.

## Results and Discussion

The curves of dependence of the magnitude of the specific magnetization of magnetite samples on the external magnetic field are shown in Fig. 1.

As can be seen (Fig. 1), the obtained dependences  $\sigma(H)$  for all the synthesized samples are very similar, almost hysteresis-free. All synthesized samples reach magnetic saturation in fields of 1500 kA/m. The magnitude of the saturation magnetization of the synthesized samples differs significantly. The use of an excess solution of ammonium hydroxide allows to obtain a system of magnetite particles the saturation magnetization of which exceeds almost three times this parameter for particles synthesized using alkali solutions.

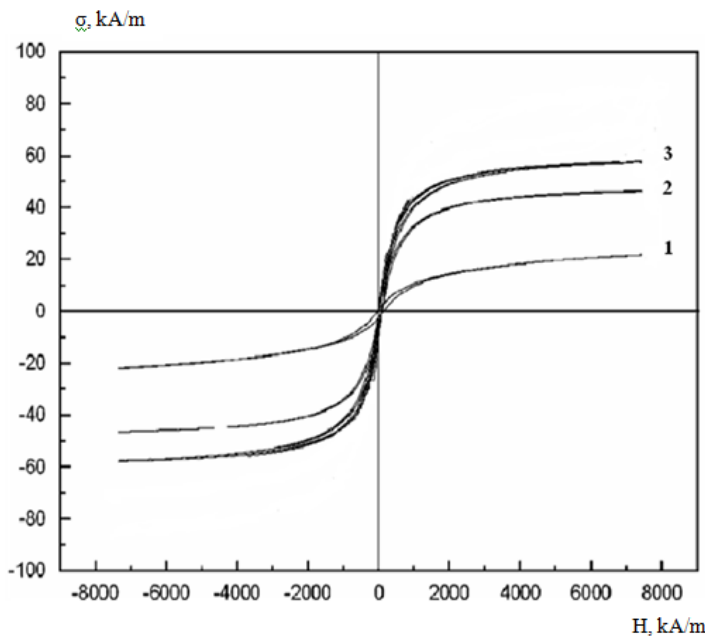


Figure 1: Hysteresis loops of the magnetite particle system, synthesized under different conditions: 1 - using KOH (or NaOH) solutions with excess  $\text{Fe}^{2+}$  (1.75); 2 - using a solution of  $\text{NH}_4\text{OH}$  at a stoichiometric ratio  $\text{Fe}^{3+} / \text{Fe}^{2+}$  2:1; 3 - using  $\text{NH}_4\text{OH}$  solution with  $\text{Fe}^{2+}$  excess (1.75)



When using alkaline solutions in a molar ratio  $[\text{OH}^-]/([\text{Fe}^{2+}] + [\text{Fe}^{3+}]) = 1.5$ , Fe(II) – Fe(III) is a double-layer green hydroxide (Green Rust) is obtained with the general formula  $[\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2\text{O}_4(\text{OH})_{12}]^{2+}$ , whose structural composition and magnetic properties are different from magnetite.

The use of a solution of ammonium hydroxide creates a soft co-precipitation conditions of iron cations, which facilitates the reaction with the formation of a very fine magnetite composition  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_2\text{O}_3 \cdot \text{FeO}$ , which has high magnetic characteristics.

Excess starting materials (ammonium hydroxide) can completely shift the equilibrium toward the formation of magnetite sediment. It should also be noted that the use of an excess of iron (II) salt leads to an improvement in the magnetic properties of the synthesized magnetite nanoparticles. Because of the strong activity of iron (II) cation. As a result of the experimental studies, the optimal conditions for the synthesis of a magnetite nanoparticle system with high magnetic properties were established. Synthesis should be carried out using a iron (III) salt and an excess 1.75 of iron(II) salt, ammonium hydroxide solution 10-10.5 excess at pH = 10-11.

In order to confirm the spinel structure of the synthesized magnetite particles, X-ray structural studies were performed. Analyzing the results of the X-ray phase analysis, it can be established that the main bands (Fig. 2) correspond to the magnetite with the spinel structure and the crystal lattice parameters of 0.83716 (4) nm. In general, the X-ray analysis (Fig. 2) showed that the experimental sample can be certified as a highly dispersed spinel system with an average particle size of ~ 16 nm.

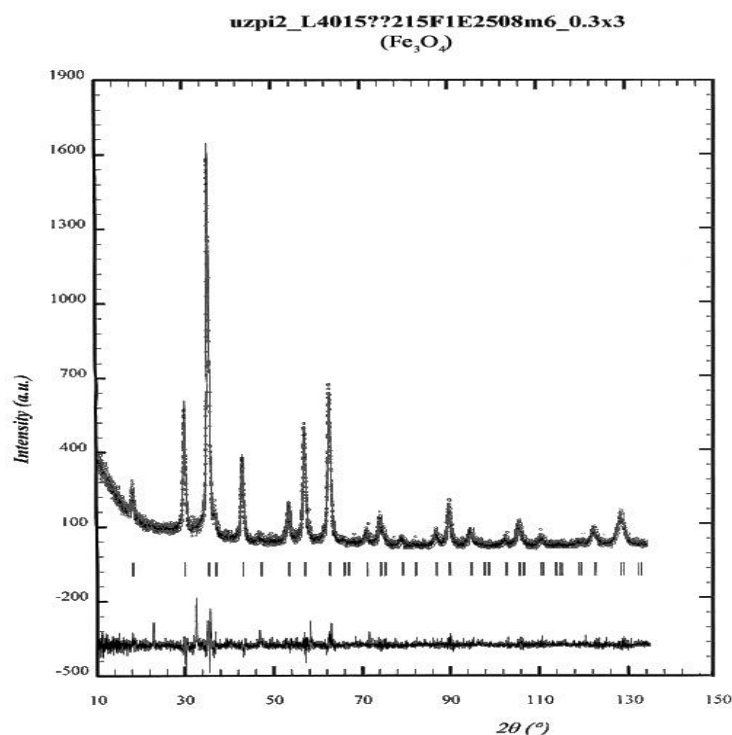


Figure 2: X-ray diffraction pattern of the sample

The X-ray of the experimental sample shows a broadening of the bands, which may indicate a slight intensity of the crystal structure of the particles. This may affect the increased ability of this sample to form colloidal solutions. The established effect can be associated with a small cation deficiency in both tetrahedral and octahedral positions, which can be estimated at about 5%, but in general, based on the task of magnetic colloid synthesis, is quite important and valuable.

On the spectrum, there are three sufficiently readable bands that indicate the presence of a small amount of substance with a highly symmetrical crystalline lattice that can be identified as an impurity.



## Conclusions

The optimal conditions for the synthesis of magnetite nanoparticles with high magnetic properties were determined experimentally (study of the dependence of the magnetization value of the synthesized samples on the magnitude of the external magnetic field). The use of an excess solution of ammonium hydroxide allows obtaining a system of magnetite particles, the saturation magnetization of which exceeds almost three times this parameter for particles synthesized using alkali solutions. It was found that the synthesis should be carried out with the use of excess of 1.75 iron (II) salt in ammonium hydroxide at pH = 10-11.

It was proved that the chosen method of synthesis allows to obtain particles of colloidal magnetite size without impurities with the correct parameters of the crystal lattice that can be used to create drugs with magnetic properties.

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