

One-pot preparation of magnetic chitosan beads

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A new one-pot method for preparation of magnetic chitosan beads comprising *in situ* prepared magnetite nanoparticles was proposed. The main advantage of the proposed method is the simultaneous obtaining of the ferromagnetic material and formation of chitosan beads by combination of two methods – the sol-gel method and capillary extrusion. In addition, appropriate conditions for effective involving of pre-formed suspension of magnetic nanoparticles into chitosan beads without losses of magnetic material during the extrusion were found. Moreover, the sol-gel method allowed considerable amounts of magnetite to be incorporated in the beads. The equilibrium swelling degree of the prepared beads depended on pH of the medium. Optical and scanning electron microscopy revealed that the core of the beads had highly porous structure. The measurements of the magnetization of the beads showed that saturation could not be reached even at a maximum external magnetic field of 6 kOe. The Mössbauer analyses revealed that the *in situ* formed magnetic nanoparticles were in superparamagnetic state and a part of them was in intermediate state between superparamagnetic and ferrimagnetic one.

Key words: chitosan, magnetic nanoparticles, superparamagnetic state, sol-gel method.

INTRODUCTION

Chitosan as a natural polysaccharide derived from renewable sources is one of the most studied biopolymers with significant potential for different applications including medical, pharmaceutical and biotechnological applications because of its good biocompatibility, biodegradability and low toxicity [1]. The appropriate involving of magnetic material in chitosan-based materials would enlarge the areas of its possible application, e.g. for fast and easy separation of microorganisms, as magnetic drug-targeting carriers, contrast enhancement agents in magnetic resonance imaging, etc. That is why chitosan has recently attracted increasing interest as carrier in magneto-sensitive materials.

The emulsion-phase-separation technique consisting in formation of a water-in-oil emulsion with the use of a surfactant has been reported for preparation of magnetic chitosan beads [2–5]. However, the size and morphology of the prepared beads depend on numerous factors such as temperature, stirring rate, concentration of the surfactant, viscosity of the phases, etc. which might limit their application. Recently, we have proposed a novel effective route for preparation of magnetic chitosan

beads by mechanical incorporation of micro- (2 μm) and nanosized (10 nm) powder of magnetic material, varying the weight ratios of chitosan:Fe₃O₄ from 4:1 to 1:1 [6]. The main disadvantage of that method is the loss of ferromagnetic material because of its sedimentation during the beads formation which leads to obtaining of beads with non-uniform amounts of Fe₃O₄.

The present work reports on a new one-pot method for fabrication of magnetic chitosan beads. The combination of the sol-gel method and capillary extrusion allows nanosized magnetite to be obtained simultaneously with the formation of the beads thus circumventing the loss of magnetite.

EXPERIMENTAL

Materials

Chitosan from crab shells (MW = 6×10^5 with 80% deacetylation degree) and glutaraldehyde (50% aqueous solution) were purchased from Fluka. Iron(III) chloride hexahydrate (97%), iron(II) chloride tetrahydrate (99%) and ammonium hydroxide (25% in water) were supplied by Aldrich. All salts used for the preparation of buffer solutions were of analytical grade. The following buffer solutions were used: pH 4.0 (CH₃COOH/NaOH), pH 7.0 (KH₂PO₄/Na₂HPO₄) and pH 9.0 (NaHCO₃/Na₂CO₃).

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All other chemicals were of analytical grade and used without further purification.

Preparation of magnetic chitosan beads

Two types of magnetic chitosan beads – with *in situ* prepared or pre-formed nanosized magnetite – were prepared. For preparation of chitosan beads with *in situ* prepared nanosized magnetite, further denoted as Ch/Fe₃O₄ (*in situ*), solution containing 40 ml of 0.4% chitosan solution in 0.4 M HCl, 0.05 M FeCl₂ and 0.1 M FeCl₃ was prepared. The obtained homogeneous solution was filtered and dropped through capillary (diameter 0.5 mm) into ammonium hydroxide precipitation bath (2.9 M NH₃), containing 0.026 M Na₂SO₃. The prepared Ch/Fe₃O₄ (*in situ*) beads were kept in the precipitation bath for 24 h and then were repeatedly washed with deionized water to neutral reaction of the aqueous phase. A part of the beads were cross-linked with glutaraldehyde (GA) in aqueous solution of GA (0.03 M) at mole ratio [GA]:[aminoglucoside units] = 5:1 at 28°C for 1 h. The crosslinked beads were washed repeatedly for removing any unreacted crosslinking agent. The beads, before and after crosslinking, were dried to constant weight at room temperature.

For comparison, beads with pre-formed magnetite were prepared. For convenience, these beads are further denoted as Ch/Fe₃O₄. In a typical run, pre-formed dispersion of magnetic nanoparticles was prepared as previously described [7]. Briefly, 1 ml of degassed solution of FeCl₂ (2 M FeCl₂ in 2 M HCl, 0.002 mol) and 4 ml of degassed solution of FeCl₃ (1 M FeCl₃ in 2 M HCl, 0.004 mol) were mixed under nitrogen and vigorously stirred. Then 50 ml degassed solution of 0.7 M NH₃ was added dropwise under nitrogen. Magnetite, as a black precipitate was immediately formed and after repeatedly washing by degassed water, magnetite suspension (14 mg/ml) was prepared by ultrasonic dispersion in degassed water. Then, under vigorous stirring, 10 ml of preformed suspension were added to 10 ml of 3% chitosan solution in 1% CH₃COOH. The obtained homogeneous viscous chitosan suspension was dropped through a capillary (diameter 0.5 mm) into 5% NaOH, thus causing formation of coacervate chitosan beads. After 24 h staying in the precipitation bath, they were repeatedly washed with deionized water to neutral reaction of the aqueous phase. The prepared Ch/Fe₃O₄ beads were cross-linked in aqueous solution of GA (0.03 M) at 28°C for 1 h at a mole ratio [GA]:[aminoglucoside units] = 5:1.

Characterization

Beads surface and core morphology was observed

by scanning electron microscope (SEM) Jeol JSM-5510. Specimens, preliminary freeze-dried, were placed on the sample holders and vacuum-coated with gold in Jeol JFC-1200 fine coater. The IR-spectra were taken with a FTIR Bruker Vector 22 spectrophotometer on a KBr plate. Thermogravimetric analyses (TGA) were carried out under nitrogen with a TA Instruments Q500 thermogravimetric analyzer in the 25–1000°C range, at a 10 °C/min rate (HiRes method). The equilibrium swelling degree (α_{eq}) of the magnetic beads was determined gravimetrically by immersion of dry and previously weighed beads in buffer solutions (pH 4, 7 and 9 and constant ionic strength $I = 0.1$) at 25°C. Then, the beads were weighed at regular intervals of time after gentle removing of the excess of buffer solution. The procedure was repeated until reaching a constant weight of the swollen beads. The α_{eq} was estimated by the equation: $\alpha_{eq} = [(w_{eq} - w_d)/w_d] \times 100$ (in %), where w_{eq} and w_d were the weights of the sample in equilibrium swollen and in dry state, respectively. The results are averages from three measurements. Phase composition and particle size of the Ch/Fe₃O₄ (*in situ*) beads were studied by X-ray powder diffraction (XRD) analysis. XRD spectra were recorded at room temperature with computer controlled D8 Bruker Advance powder diffractometer with a filtered Cu-K α radiation and a scintillation registration. Data were collected in the 2 θ range from 5 to 85° with a step 0.02° and counting time of 1 s/step. The magnetization of the Ch/Fe₃O₄ (*in situ*) beads was measured with a vibrating-sample magnetometer by applying an increasing magnetic field. Dry beads were fixed in quartz holders, which were placed in the magnetometer. The Mössbauer spectroscopy analysis was performed in a transmission mode with conventional constant acceleration spectrometer at 300 and 77K. A ⁵⁷Co source in an Rh matrix with a diameter of the activity spot of 5 mm was used. The spectra were fitted using continuously magnetic field distribution and quadrupole splitting distribution. The isomer shifts of the spectra are referred to the centroid of α -Fe foil reference spectrum at room temperature. The dried beads were pulverized in a mortar, mixed with PVA powder (glue substance) and pressed into a disk.

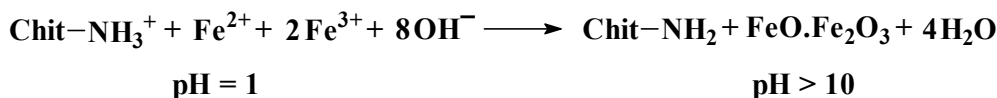
RESULTS AND DISCUSSION

Preparation and characterization of magnetic chitosan beads

One-pot preparation of magnetic chitosan beads comprised *in situ* prepared nanosized magnetite by combining the sol-gel and simple coacervation methods. Simultaneous formation of the nanosized

magnetite and beads, which occurs during the extrusion of the mixed chitosan, FeCl₂ and FeCl₃

solution into the alkaline precipitation bath, is due to the following reaction:



During the capillary extrusion of the chitosan/FeCl₂/FeCl₃ solution into ammonium hydroxide bath, the conversion of the water-soluble protonated form (-NH₃⁺) of chitosan to the water-insoluble neutral (-NH₂) form takes place. This leads to the simultaneous formation of beads and coprecipitation of FeCl₂ and FeCl₃, thus forming nanosized magnetite (Fe₃O₄). For comparison of the obtained Ch/Fe₃O₄ (*in situ*) beads, cocervate chitosan beads with pre-formed magnetite were prepared. This is a two-step process including preliminary preparation of nanosized magnetic suspension, followed by adding of this suspension to chitosan solution and subsequent extrusion of the obtained chitosan suspension into alkaline precipi-

tation bath. This way of preparation (using Fe₃O₄ suspension) is more advantageous than involving magnetite powder since it allows better homogenization of the solution and thus minimizes the losses of magnetic material during the extrusion process.

The morphology of the beads surface and core was observed by SEM after freeze-drying. As seen from the SEM micrographs (Fig. 1), the surface of the prepared beads is smooth, while their cross-section reveals highly porous structure, characteristic of chitosan. The measurements showed that the pore size of the Ch/Fe₃O₄ beads (45 μm) was considerably larger than that of Ch/Fe₃O₄ (*in situ*) beads (1.8 μm).

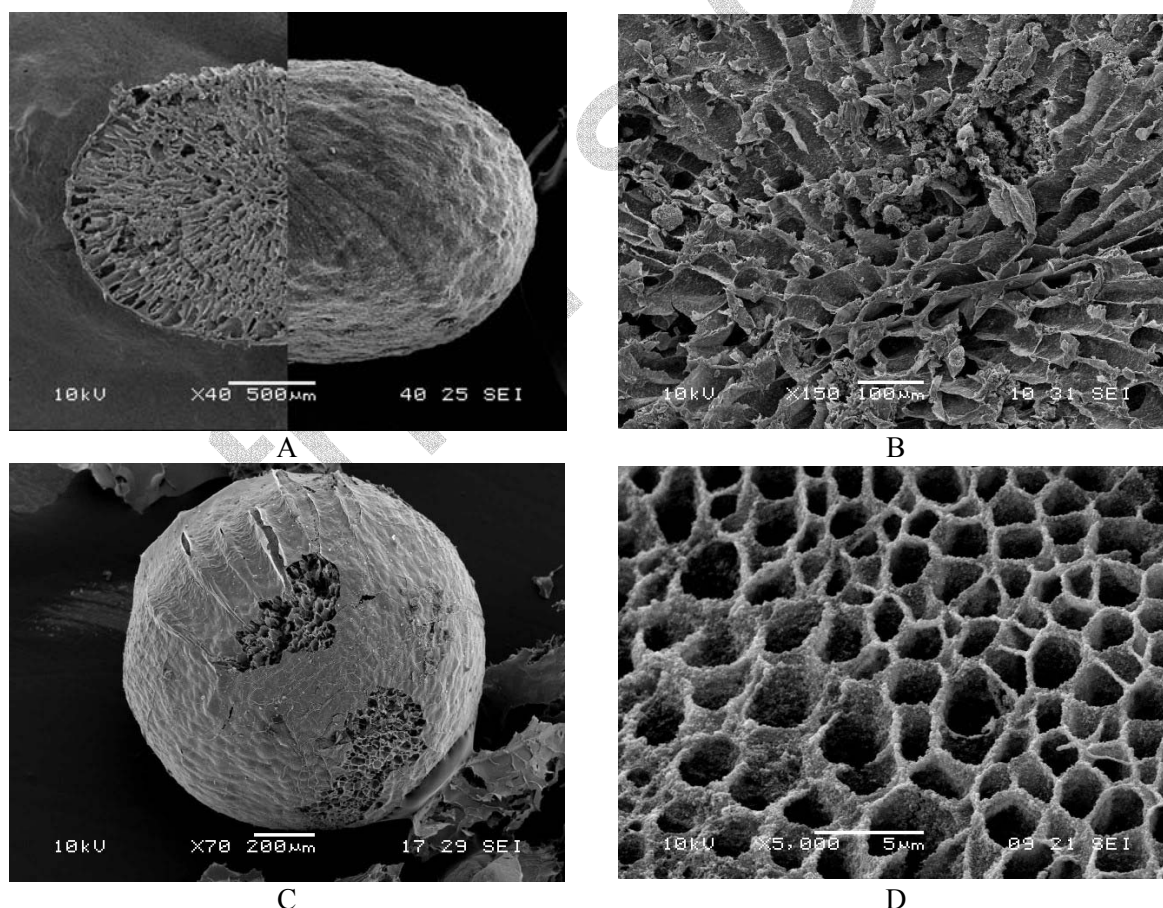


Fig. 1. SEM micrographs of freeze-dried magnetic chitosan beads: Ch/Fe₃O₄ ×40 (A) and ×150 (B); Ch/Fe₃O₄ (*in situ*) ×70 (C) and ×5 000 (D).

The IR spectra of the beads showed the following characteristic for chitosan bands: in the range of 3500–3300 cm⁻¹ (NH- and OH-stretching

vibrations), the bands due to its saccharide structure – at 1153 cm⁻¹ (OH-bending), 1068 cm⁻¹ (-C-O-C- stretching vibrations) and 1030 cm⁻¹ (OH-bending)

and for Amide I at 1634 cm^{-1} . A new band in the low-frequency region ($570\text{--}588\text{ cm}^{-1}$), due to the iron oxide skeleton ($-\text{Fe}-\text{O}-$ stretching vibrations), is an evidence for presence of magnetite in the beads [8].

The changes which occur after thermal treatment of $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) beads were estimated by TGA (Fig. 2). The most considerable destruction (approximately 32% weight losses) was observed in the range of $150\text{--}780^\circ\text{C}$. As seen, the first decomposition stage started at 150°C and ended at 420°C with weight loss of 15.8% from the sample initial weight. The second stage continued up to 780°C with weight losses of 15.9%. Clearly, these two stages correspond to the thermal decomposition of chitosan, which usually starts at 250°C and ends at 650°C [9].

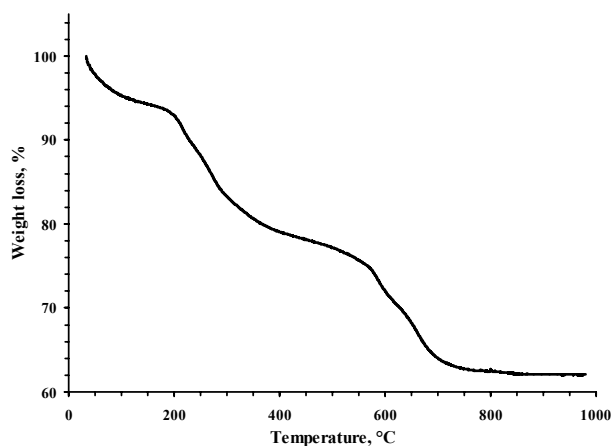


Fig. 2. TGA thermogram of dried $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) beads

The successful preparation of $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) beads enriched in Fe_3O_4 has been evidenced by all these previous experiments. Moreover, the one-pot preparation of $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) beads provides an additional possibility for their stabilization which is favored by the complex formation between amino groups of chitosan and iron ions [10, 11]. Therefore, the formation of physical network during the extrusion process leads to collapse of chitosan gel, thus decreasing the pore size of $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) beads compared to $\text{Ch}/\text{Fe}_3\text{O}_4$ one. These peculiarities of the one-pot preparation of $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) beads determine different behaviour of the beads at different pH values. The dependence of the equilibrium swelling degree (α_{eq}) of the $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) and $\text{Ch}/\text{Fe}_3\text{O}_4$ beads on the pH (4, 7 and 9) of the medium is presented in Table 1. As seen, the highest α_{eq} value (exceeding 1000%) was attained in acidic medium for the $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) beads. After 6 h at pH 4 the $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) beads fragmented, thus hampering the determination of α_{eq} at this pH value. At pH 4 $\text{Ch}/\text{Fe}_3\text{O}_4$ beads dissolved

in comparison with $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*). As seen (Table 1), the $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) and $\text{Ch}/\text{Fe}_3\text{O}_4$ beads swelled slightly at pH 7 and pH 9, besides $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) swelled less than $\text{Ch}/\text{Fe}_3\text{O}_4$ beads.

Table 1. Dependence of the equilibrium swelling degree (α_{eq}) of different magnetic chitosan beads on pH; 25°C ; $I = 0.1$.

Beads	α_{eq} , %		
	pH = 4	pH = 7	pH = 9
$\text{Ch}/\text{Fe}_3\text{O}_4$ (<i>in situ</i>)	1300 ^a	24	16
$\text{Ch}/\text{Fe}_3\text{O}_4$ (<i>in situ</i>)/GA	212	16	15
$\text{Ch}/\text{Fe}_3\text{O}_4$	^b	125	162
$\text{Ch}/\text{Fe}_3\text{O}_4$ /GA	255	64	41

^a the beads are fragmented after 6 h; ^b the beads are dissolved.

As mentioned above, due to the formation of physical network by interaction between the amino groups of chitosan and iron ions in $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) the pore size decreased thus decreasing the water uptake in the beads. After chemical cross-linking with glutaraldehyde (GA), both beads types were stable in acidic medium and reached equilibrium swelling degree for 24 h. Obviously, non-crosslinked beads swelled to a greater extent compared to the crosslinked ones and the α_{eq} values were higher in acidic than in neutral or alkaline solutions (Table 1). For example, at pH 7 the α_{eq} decreased in the order: $\text{Ch}/\text{Fe}_3\text{O}_4 > \text{Ch}/\text{Fe}_3\text{O}_4/\text{GA} > \text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) $> \text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*)/GA. For the beads, crosslinked with GA, α_{eq} decreased in the order: pH 4 $>$ pH 7 $>$ pH 9.

The obtained results show the advantages of the one-pot preparation of magnetic chitosan beads. Further, the magnetic properties of the beads were studied.

Magnetic properties of the prepared magnetic chitosan beads

The presence only of magnetite (Fe_3O_4) phase was confirmed by XRD analysis of dried $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) beads (Fig. 3). The iron oxide phase was identified from the XRD patterns by the peak positions at 18.2 (111), 30.0 (220), 35.5 (311), 43.1 (400), 53.4 (422), 57.0 (511), 63 (440) and 73.9 (533), which were in agreement with magnetite standard data.

The mean particle size of the formed in the beads ferromagnetic particles was 12 nm, as calculated by the Scherer's equation. It has been reported that Fe_3O_4 particles with size lower than 20 nm are superparamagnetic [12]. Therefore, it might be assumed that a part of the magnetite, formed *in situ* in the beads, is in superparamagnetic state.

Magnetization of the $\text{Ch}/\text{Fe}_3\text{O}_4$ (*in situ*) beads as a function of internal magnetic field was measured

by vibrating-sample magnetometer (Fig. 4). As seen, the saturation of magnetization could not be reached even at maximum internal magnetic field of 6 kOe. At $H = 0$, the magnetization curve showed almost immeasurable coercivity ($H_c = 100$ Oe) and remanence ($M_r = 1.2 \pm 0.2$ emu/g). These low values of H_c and M_r showed that magnetic particles formed in Ch/Fe₃O₄ (*in situ*) beads were in superparamagnetic state [13].

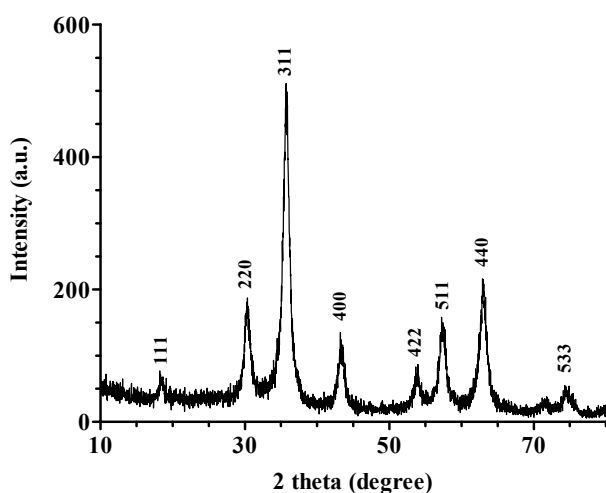


Fig. 3. XRD patterns of the dried Ch/Fe₃O₄ (*in situ*) beads.

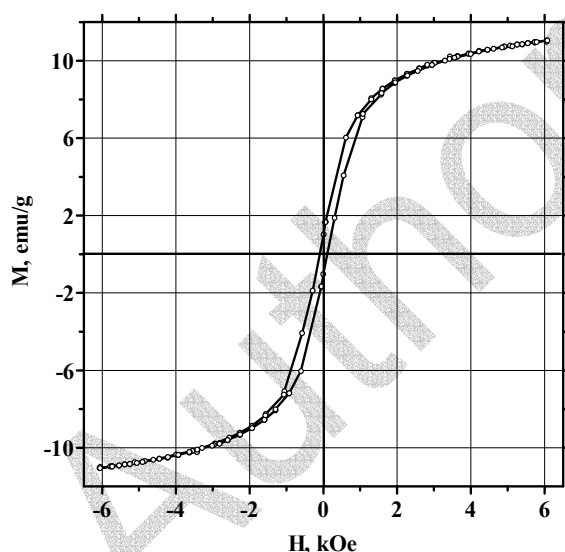


Fig. 4. Magnetization curve at 300K of the dried Ch/Fe₃O₄ (*in situ*) beads

However, the presence of immeasurable hysteresis indicated that a part of the magnetic nanoparticles existed in different magnetic states – superparamagnetic and intermediate state between superparamagnetic and ferrimagnetic one. The low value of the saturation magnetization ($\sigma_s = 11$ emu/g) proved that the magnetic particles formed in Ch/Fe₃O₄ (*in situ*) beads were as small as single magnetic domain ($D_p = 20$ nm).

The results obtained from the Mössbauer spectra confirmed the assumption of superparamagnetic properties of the obtained magnetic beads. The properties of incorporated magnetic iron oxide nanoparticles in the porous polymer matrix depend considerably on the particle size. As already mentioned, particles with dimensions lower than 20 nm are often superparamagnetic, which means that the magnetization vector fluctuates among the easy directions of magnetization (superparamagnetic relaxation) [14]. When the relaxation time τ is longer than 10^{-8} s, the Mössbauer spectra are magnetically split. For $\tau < 10^{-9}$ s, the magnetic splitting collapses and spectra with singlets or doublets are obtained. In the case, when τ is between 10^{-9} and 10^{-8} s, spectra with broadened lines are observed because the fluctuations of the magnetization direction lead to a reduction in the magnetic hyperfine splitting of the spectra.

The Mössbauer spectrum at 300K of Ch/Fe₃O₄ (*in situ*) dried beads (Fig. 5A) was fitted as superposition of two magnetic sextet's distributions and a superimposed quadrupole doublets distribution. The spectrum was typical for magnetic particles in superparamagnetic state or close to it. Actually, the magnetic splitting collapsed only for 18.7% of magnetic particles corresponding to quadrupole doublets distribution (Table 2). This component was due to the smallest nanoparticles which exhibited fast superparamagnetic relaxation ($< 10^{-9}$ s). However, the majority of nanoparticles were in intermediate region (10^{-9} s $< \tau < 10^{-8}$ s). The Mössbauer spectrum of the same sample but at liquid nitrogen temperature (Fig. 5B) was fitted as a superposition only of two magnetic sextet's distribution; its Mössbauer parameters are presented in Table 2. At this temperature (77K) the superparamagnetic relaxation was blocked for all magnetic nanoparticles, including these with the smallest diameter. Moreover, at this temperature both distributions of the magnetic field are related to Fe(II) and Fe(III), and not to octahedral and tetrahedral positions.

The reason was that the Mössbauer measurements were made under Verwey point (120K), when the electron exchange between Fe³⁺ and Fe²⁺ in octahedral positions in magnetite was absent. It was determined from the relation between the areas of both magnetic distributions that the spectrum of as-prepared magnetite might be interpreted as a spectrum of magnetite with ratio Fe³⁺/Fe²⁺ = 4. This ratio is Fe³⁺/Fe²⁺ = 2 for standard magnetite. Therefore, probably in Ch/Fe₃O₄ (*in situ*) beads a part of the Fe(II) in position B was oxidized or a part of magnetite was converted in maghemite. These results are in agreement with the values of isomer shifts listed in Table 2.

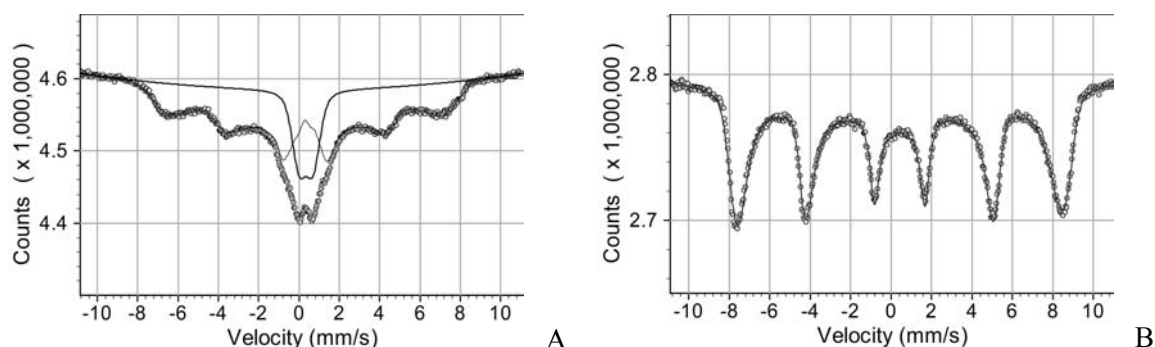


Fig. 5. Mössbauer spectra of dried Ch/Fe₃O₄ (*in situ*) beads recorded at 300K (A) and 77K (B).

Table 2. Mössbauer parameters^a of dried Ch/Fe₃O₄ (*in situ*) beads.

Sample	T ^b , K	SXT	IS, mm/s	H _{avr} , kOe	σH, kOe	H _{max} , kOe	QS _{avr} , mm/s	QS _{area} , %
Ch/Fe ₃ O ₄ (<i>in situ</i>)	300	I	0.30	296	-	436	0.78	18.7
		II	0.68	276	-	430		
	77	I	0.44	422	53	504	-	0
		II	0.37	403	52	498	-	

^a isomer shift (IS); average magnetic field at the site of the Fe nucleus (H_{avr}); dispersion of magnetic hyperfine-field distribution (σH); maximum value of magnetic hyperfine-field distribution (H_{max}); average quadrupole splitting (QS_{avr}); relative spectral area of quadrupole doublets distribution (QS_{area}); ^b T (K) - temperature in K degrees.

As seen, the results are close to literature data for maghemite [15] implying that topotactic oxidation of magnetite has taken place during storage. At room temperature the Mössbauer spectra of bulk magnetite and maghemite are quite different. When the material is in the form of nanoparticles the crucial parameter of the Mössbauer spectra to distinguish between two possible iron oxides is the isomer shift. Moreover, the isomer shift is typically ≥ 1.0 mm/s for Fe²⁺, while 0.3–0.4 mm/s for Fe³⁺. Therefore, the values of isomer shift of Ch/Fe₃O₄ (*in situ*) presented in Table 2 suggest an average valence of iron close to Fe³⁺.

CONCLUSIONS

The combination of the sol-gel method with those of simple coacervation is successfully used for one-pot preparation of chitosan beads with *in situ* involved nanosized magnetite. Compared to the beads with pre-formed nanosized magnetite, these with *in situ* prepared magnetite are more stable in acidic medium. The size of the *in situ* prepared magnetite is 12 nm, as proved by the XRD calculations and by the low values of saturated magnetization. The measurements of the magnetization and the Mössbauer analyses showed that the magnetic particles formed in the beads existed in superparamagnetic state and a part of them was in intermediate state between superparamagnetic and ferrimagnetic one. Therefore, the herein one-pot prepared Ch/Fe₃O₄ (*in situ*) beads are promising magnetic materials.

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ЕДНОЕТАПНО ПОЛУЧАВАНЕ НА МАГНИТНИ ХИТОЗАНОВИ СФЕРИ

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Посветена на акад. Иван Юхновски по повод на 70-та му годишнина

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(Резюме)

Предложен е нов едноетапен метод за получаване на магнитни хитозанови сфери, включващ *in situ* получени магнитни наночастици. Основното предимство на предложения метод е получаването на феромагнитен материал едновременно с формирането на хитозановите сфери като това става чрез комбинирането на два метода – зол-гел метода и капилярната екструзия. В допълнение, намерени са подходящите условия за ефективно включване на предварително получена суспензия от магнитни наночастици в хитозанови сфери без загуба на магнитен материал по време на екструзията на разтвора. Нещо повече, зол-гел методът позволява включването на значителни количества магнетит в сферите. Равновесната степен на набъбване на получените сфери зависи от рН на средата. Оптичната и сканираща електронна микроскопия разкриват силно порестата структура на сферите. Измерването на намагнитеността на сферите показва, че насищане не се достига дори при максимално външно магнитно поле от 6 кОе. Мьосбауеровите анализи показват, че *in situ* получените магнитни наночастици са в суперпарамагнитно състояние и част от тях са в междинно състояние – между суперпарамагнитно и феримагнитно.