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Composite magnetic chitosan microspheres: In situ preparation and characterization

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Abstract A method for preparing magnetic crosslinked chitosan microparticles was developed. The chitosan (CS) encapsulated magnetic particles were produced in alkaline conditions by in situ oxidation of the ferrous ions initially dispersed uniformly within the polysaccharide matrix. The polymer was then crosslinked using glutaraldehyde (GLA). The products were characterized regarding their size distribution and surface charge (by laser diffraction analysis, ζ-potential measurement, and conductometric titration), morphology (TEM), and magnetic properties (magnetic susceptibility analysis). The fact that the particles contain both magnetic iron oxide and chitosan was confirmed by FTIR and thermogravimetric analysis. The synthesis parameters were optimized for obtaining stable magnetic microparticles bearing surface amino groups that can subsequently be used for heavy metal ion complexation. The composite particles obtained by the optimum procedure had an average diameter of 40 μm and a saturation magnetization of 24 emu/g, corresponding to about 47% magnetic iron oxide content.

Keywords Magnetic particles · Chitosan · Iron oxide · Composite

Introduction

Water contamination with heavy metal ions is a stringent and current environmental problem due to the fact that they are not biodegradable and tend to accumulate in

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living organisms producing extremely toxic effects [1]. Conventional methods for heavy metal ion removal include chemical precipitation, membrane processes, electrochemical techniques and adsorption procedures, the latest being recognized by far as the most efficient ones [2]. Recent work in scientific research shows a high interest for new cheap, biocompatible, and biodegradable adsorbent materials based on the natural polymers, particularly polysaccharides [3]. Chitosan is derived from a natural polysaccharide (chitin), it consists of β(1-4)-2-amino-2-deoxy-D-glucan units and has excellent adsorption behavior toward metal ions, mainly due to the presence of a large number of primary amino and hydroxyl groups [4]. Despite its possible advantages, the commercial material in the form of powder or flakes is not suitable to be used directly as an adsorbent because it is soluble in acidic solutions and it has low surface area. One of the options is to prepare composite chitosan–magnetite particles with high specific surface area, easy to separate from the eluent after complexing the heavy metal ions by using a magnetic field [5].

Several methods have been developed for obtaining magnetic chitosan microspheres, such as reverse-phase suspension cross-linking method [6], in situ microemulsion method [7], and magnetite synthesis by co-precipitation followed by chitosan coating [8]. Most of them require multi-step purification procedures and have low solid yield due to the use of dilute solutions.

The aim of this work was to develop and optimize a simple one step high yield method for obtaining chitosan magnetic composite particles.

Experimental

Materials and methods

Low molecular weight chitosan (CS_LMW) ($M_w = 50$–190 kDa; degree of deacetylation 84.5%), Pluronic F-127 and sodium hydroxide were obtained from Sigma-Aldrich, Germany; ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), glutaraldehyde (GLA; 25% solution in water) and potassium nitrate (KNO_3) were purchased from Merck, Germany; aqueous ammonia solution (25% by weight), glacial acetic acid (CH_3COOH) and hydrochloric acid (1 N aqueous solution) were procured from Chemical Company (Iasi, Romania).

Reagents have been used as purchased, without further purification. All solutions were prepared with de-ionized water.

In situ preparation of magnetic chitosan particles

Magnetic CS composite particles were obtained by in situ method. The magnetic materials were formed by mild oxidation of the ferrous ion, entrapped in a chitosan–Fe(II) complex, using nitrate ion as a mild oxidizing agent, under alkaline conditions.

Briefly, CS was dissolved in 1 M glacial acetic acid to prepare a solution of 2, 3, or 4% concentration, respectively. This solution was transferred into an Erlenmeyer flask containing the required amount of aqueous $FeCl_2 \cdot 4H_2O$ solution. The mixture

Table 1 Synthesis parameter study

Batch	CS/Fe(II) ratio (g/g)	CS conc. (%)	Ammonia sol. conc. (M)	GLA conc. (%)	D_v (μm)	D_n (μm)
Mag_IS C1	0.9:1	3	0.5	2.5	30	6
Mag_IS_C3	0.9:1	3	0.5	5	40	21
Mag_IS_C3_1	0.9:1	3	0.5	5	39	19
Mag_IS_C3_2	0.9:1	3	0.5	5	45	26
Mag_IS C4	0.9:1	3	0.5	10	76	45
Mag_IS D	0.9:1	3	0.25	5	40	35
Mag_IS E	0.9:1	3	0.75	5	27	11
Mag_IS F	0.9:1	2	0.5	5	68	6
Mag_IS G	0.9:1	4	0.5	5	74	6

was homogenized by ultrasonication under reduced pressure for 15 min. It was then precipitated in a three-necked round bottom flask placed in a water bath by the addition of aqueous ammonia solution in nitrogen atmosphere, using a peristaltic pump (flow rate 10 ml/min), under mechanical stirring.

The resulting dark-green CS–$Fe(OH)_2$ complex was stirred for an hour in a thermostated water bath kept at 70 °C. The mixture was then oxidized using aqueous 10% KNO_3 solution and aged under stirring for another hour at the same temperature. The obtained dark black particles were collected by sedimentation and washed repeatedly until neutral pH using magnetic field separation for aqueous supernatant removal. The particles were then dispersed in 200 ml water. A non-ionic surfactant, Pluronic F-127, was added (10 ml of 2% aqueous solution). The CS matrix was crosslinked by addition of 30 ml aqueous GLA solution with 2.5, 5, or 10% concentration (as shown in Table 1), under mechanical stirring, at room temperature, for 30 min. In order to remove leftover crosslinker, the particles were washed with 3 × 200 ml water. An acid–base treatment followed by dialysis against distilled water for 3 days completed the cleaning procedure.

A dispersion aliquot was dried at 105 °C (using a Mettler-Toledo HG63 moisture analyzer) and kept for further analysis. The remaining wet aqueous dispersion was stored at 4 °C.

In situ synthesis of bare magnetic particles

Bare magnetic material (Mag_P) was obtained by the same method without the polysaccharide matrix. This sample was used in analysis as blank material.

Characterization

The morphology of the composite particles was investigated by Transmission Electron Microscopy (TEM) on a dry sample. Particle size distribution was measured on an aqueous sample dispersion using a laser diffraction analyzer (Shimadzu SALDI-7001). The magnetization was determined on a VSM 7410 vibrating sample magnetometer. Qualitative chemical composition assessment was performed by FTIR analysis (Bomem MB 104 spectrometer). Thermogravimetric analysis was carried out on a Metller Toledo TGA-SDTA851 system, in nitrogen atmosphere, at a heating rate of 10 K/min and sample weight of 4–5 mg. Zeta potential was measured in phosphate buffer with pH 6 (all the amino groups belonging to chitosan are protonated at pH lower than 6.3 [4]) on a Malvern Zetasizer ZS90 system.

The concentration of the surface amino groups was assessed by conductometric titration, using a concentrated particle suspension (0.309 g in 30 ml), with pH adjusted to 6.7. The suspension was titrated with 0.01 N HCl, while monitoring the conductivity with a Consort C831 analyzer.

Results and discussions

The magnetic material was obtained under alkaline conditions by oxidation of the ferrous ions complexed within the polysaccharide matrix using nitrate as a mild oxidizing agent, according to the chemical reaction shown below:

$$12\mathrm{Fe(OH)_2} + \mathrm{NO_3^-} \rightarrow 4\mathrm{Fe_3O_4} + \mathrm{NH_3} + 10\mathrm{H_2O} + \mathrm{OH^-}.$$

Further oxidation may lead to other iron oxides such as γ-Fe_2O_3 (maghemite) or α-Fe_2O_3 (hematite).

The Fe(II) salt was first dispersed into the CS solution in acidic conditions. While the pH increased upon ammonia addition, CS solubility decreased and it precipitated into particles. At the same time, divalent iron ions complexed with amino groups belonging to the CS matrix, ensuring uniform incorporation [9]. Finally, encapsulated magnetic iron oxide was formed in situ by oxidation.

The composite particles were then cross-linked with GLA to avoid particle dissolution in acidic media.

Synthesis parameter study

The synthesis parameters were optimized to yield stable particles with uniform size distribution. The average volumetric (D_v) and numeric (D_n) particle size obtained for lots prepared under various conditions are shown in Table 1.

The composite particles obtained by the optimum procedure had an average diameter of 40 μm (Mag_IS_C3). Batches designated as Mag_IS_C3, Mag_IS_C3_1, and Mag_IS_C3_2 are synthesized under the same conditions (optimum) and the results are comparable by dimensions (between 39 and 45 μm), proving that the procedure is reproducible as shown in Fig. 1. This size range is suitable for easy separation and regeneration of the magnetic particles.

Magnetization measurements

The magnetization curves obtained for bare magnetic material and composite particles are presented in Fig. 2. The magnetic saturation was 51.07 emu/g for the

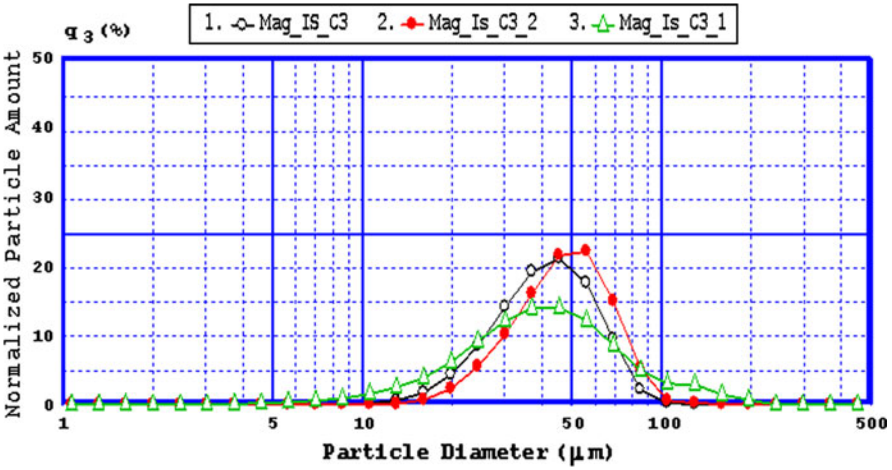

Fig. 1 Size distribution (volumetric average) of composite particles (Mag_IS_C3, Mag_IS_C3_1, and Mag_IS_C3_2)

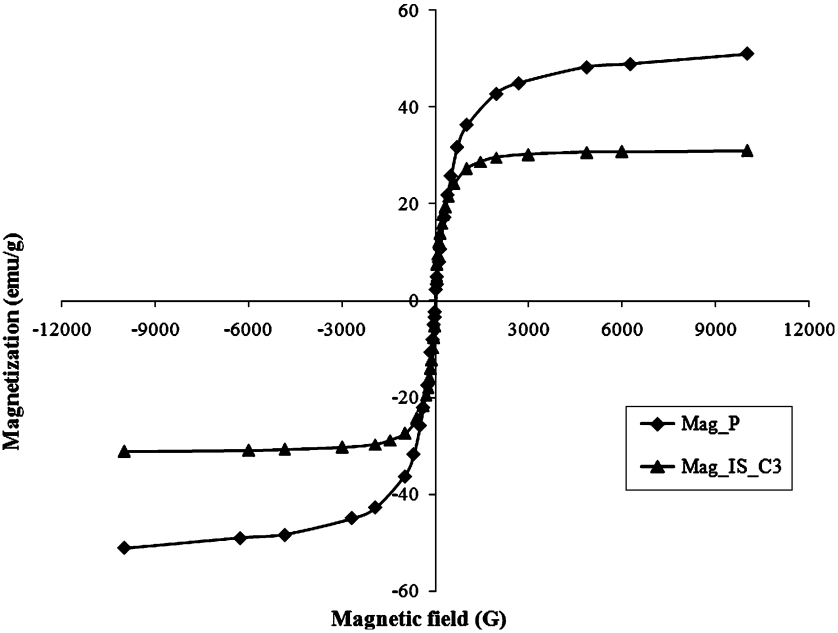

Fig. 2 Magnetization curves for composite particles and bare magnetic material

bare magnetic material (Mag_P) and 24 emu/g for the CS magnetic particles (Mag_Is_C3) obtained by the optimum procedure, corresponding to about 47% magnetic material content in the composite particles.

FTIR analysis

Figure 3 shows the FT-IR spectra of bare magnetic material, CS and magnetic CS composite particles (batch Mag_IS_C3). The peak located around 3,430 cm^{-1} is related to the –OH group. For bare magnetic material, the peak at 576 cm^{-1} is assigned to Fe–O group. For the IR spectrum of raw CS, the band of 1,637 cm^{-1} was assigned to N–H bending vibration and the peak of 1,382 cm^{-1} to –C–O stretching of primary alcohol group. In the spectrum of composite particles, the 1,637 cm^{-1} peak of N–H bending vibration remains the same and the 1,382 cm^{-1} peak characteristic to –C–O bending vibration is shifted to 1,375 cm^{-1}, due to crosslinking with GLA.

The characteristic peak for Fe–O group is located at 603 cm^{-1} in the composite spectrum. All characteristic peaks of CS were also present in the spectrum of composite particles. The results indicated that the product contains both iron oxide and CS. The spectra are comparable to other results presented in the literature [10].

Thermogravimetric analysis

The fact that the resulting particles contain both iron oxide and CS is also confirmed by the thermogravimetric analysis, presented in Table 2.

For each sample (CS_LMW, Mag_P, and Mag_IS_C3), the peak temperature at which the degradation is maximum in each step, its percentage weight loss, and the amount of residue that is left after heating the samples to 900 °C are shown in this

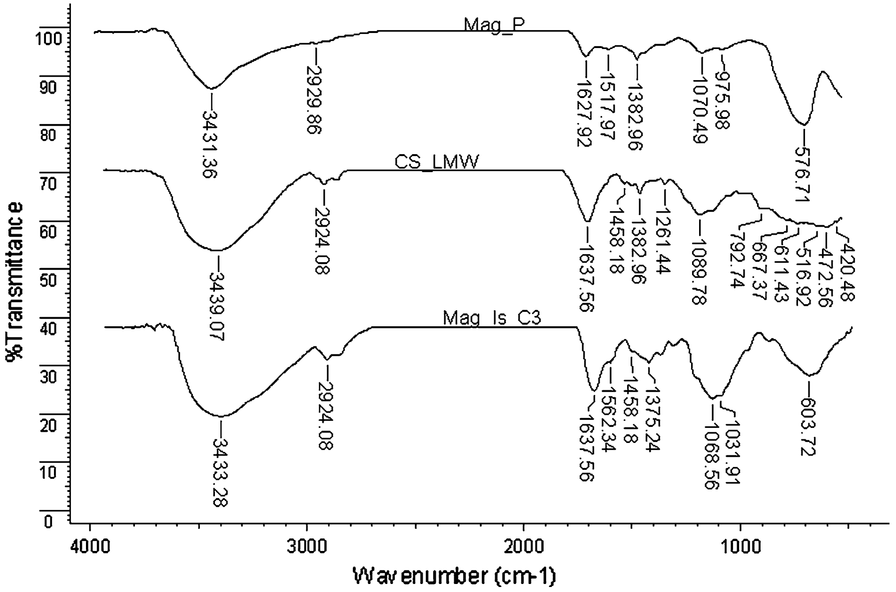

Fig. 3 IR spectra for bare magnetic material (Mag_P), CS (CS_LMW) and composite particles (Mag_IS_C3)

Table 2 Thermogravimetric analysis

Sample	Step	T_{peak} (°C)	wt%	Residue%
CS_LMW	I	66	7.50	27.35
	II	318	65.15	
Mag_P	I	106	0.58	91.81
	II	427	5.33	
	III	620	2.28	
Mag_IS_C3	I	79.3	12.38	31.77
	II	258	22.35	
	III	432	12.38	
	IV	684	21.12	

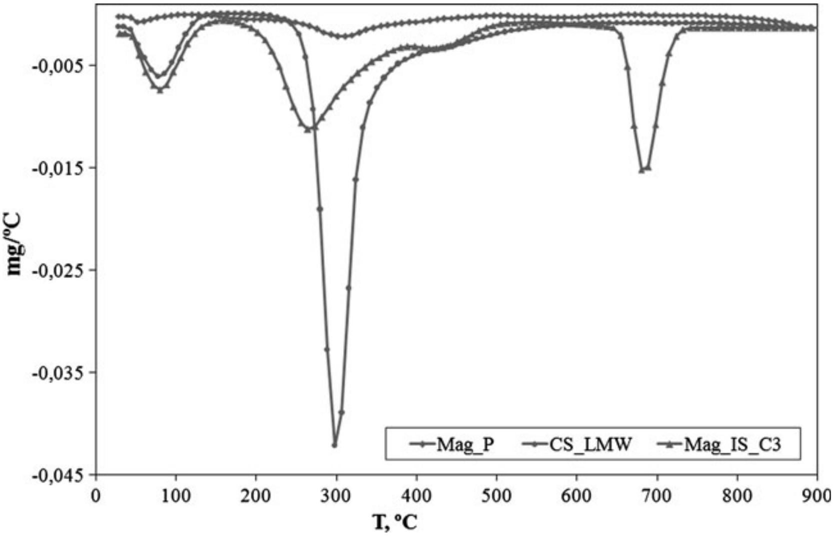

Fig. 4 DTG curves of chitosan (CS_LMW), bare magnetic material (Mag_P), and composite particles (Mag_IS_C3)

table. Comparative differential thermogravimetric curves of the same samples are presented in Fig. 4.

The results show that all samples eliminate water in the range of 56 to 106 °C. The bare magnetic material prepared in situ has a hydrophilic character and it shows little weight loss when heated up to 900 °C. The second stage, occurring at 427 °C, is probably due to formation of some amorphous oxide. The maximum thermal decomposition of CS_LMW occurs at 318 °C. By comparison, the composite material shows a second decomposition step at lower temperature, 258 °C, probably due to the fact that the CS matrix obtained by alkaline precipitation from solution has lower crystallinity than the raw material. The third and fourth step, occurring at 432 and 684 °C, respectively, are probably related to the decomposition of a highly crosslinked CS fraction, as well as to the presence of some amorphous iron oxide.

Microscopy

TEM micrographs for the composite particles (batch Mag_IS_C3) are shown in Fig. 5. The pictures show distinct iron oxide nanoparticles that are finely dispersed within the polysaccharide matrix. The lack of agglomeration phenomena (which would result in mutual magnetization cancellation) explains the high magnetization of the resulting composite material.

The results are similar to other data reported in the literature [8, 11].

Surface properties

Comparative results for ζ-potential measurement and the conductometric titration are shown in Table 3.

The bare magnetic particles are negatively charged probably due to the presence of adsorbed hydroxyl ions. By comparison, the CS-encapsulated iron oxide becomes positively charged.

The concentration of the surface amino groups was estimated by conductometric titration and the curve is presented in Fig. 6. At the beginning of titration all the

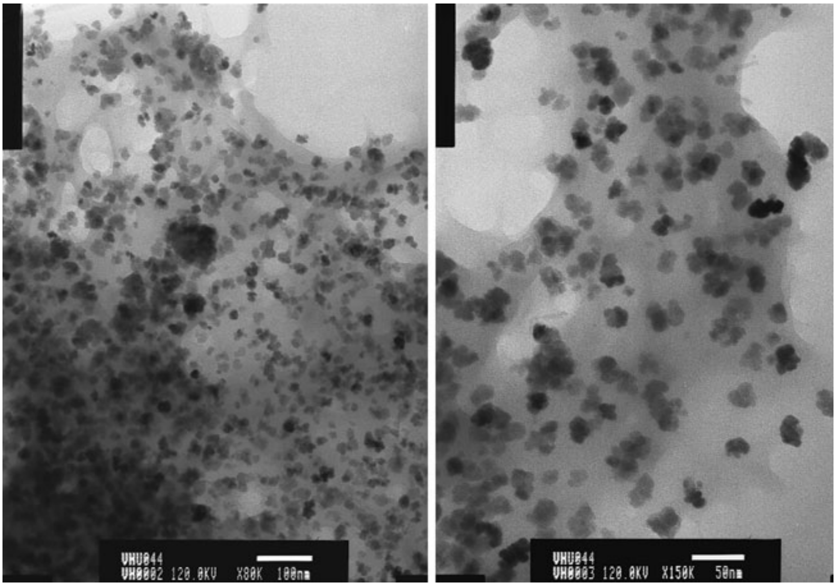

Fig. 5 TEM images of composite particles (Mag_IS_C3)

Table 3 Surface properties

Batch	ζ-potential (mV)	NH_2 groups (mole/g)
Mag_P	−12.7	–
Mag_IS_C3	+1.09	3.94×10^{-4}

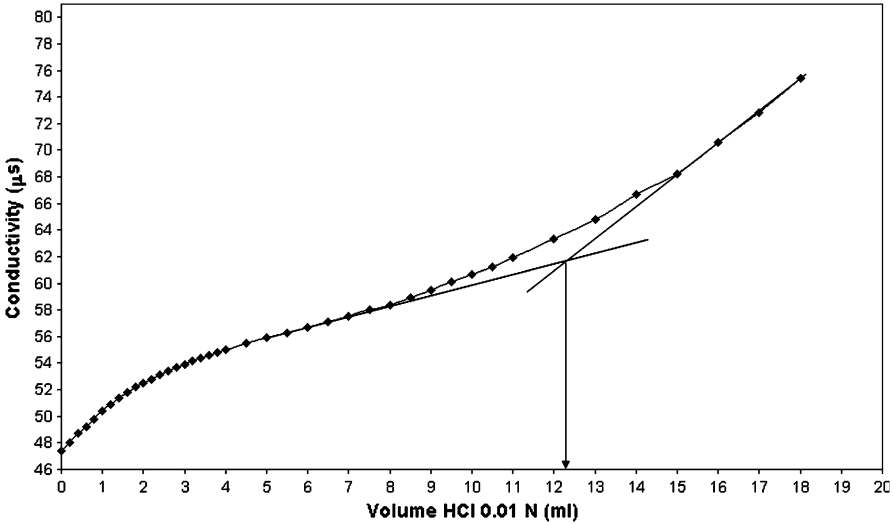

Fig. 6 Conductometric titration curve

amino groups belonging to chitosan are in NH_2 form. By adding hydrochloric acid to the sample it reacts with the surface NH_2 groups and the conductivity remains constant. Once all the amino groups have been protonated, any excess acid causes an increase in conductivity. The results prove that composite particles bear free surface amino groups available for complexing with heavy metal ions.

Conclusions

A simple method for preparing magnetic chitosan composite microparticles using in situ method was developed and optimized. The particles obtained in a reproducible manner by the optimum procedure had an average diameter of 40 µm with the saturation magnetization of 24 emu/g. TEM micrographs show that finely dispersed iron oxide nanoparticles were successfully encapsulated into the polymeric matrix, as confirmed also by FTIR and thermogravimetric analysis. The composite particles bear free surface amino groups that were evidenced by conductometric titration and ζ-potential measurements. These groups can be used for heavy metal ion complexation.

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References

1. Manahan SE (2001) "Water Pollution" fundamentals of environmental chemistry, 2nd edn. CRC Press LLC, Boca Raton

2. Barakat MA (2010) New trends in removing of heavy metals from industrial wastewater. Arab J Chem. doi:10.1016/j.arabjc.2010.07.019
3. Crini G (2005) Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Prog Polym Sci 30:38–70
4. Guibal E (2004) Interactions of metal ions with chitosan-based sorbents: a review. Sep Purif Technol 38:43–74
5. Hu Y, Bo Y, YaoBo L, RongShi C (2009) Preparation of magnetic chitosan microspheres and its applications in wastewater treatment. Sci China Ser B Chem 52:249–256
6. Zhao D-L, Wang X-X, Zeng X-W, Xi Q-S, Tang J-T (2009) Preparation and inductive heating property of Fe3O4–chitosan composite nanoparticles in an AC magnetic field for localized hyperthermia. J Alloy Compd 477:739–743
7. Jia Z, Yujun W, Yangcheng L, Jingyu M, Guangsheng L (2006) In situ preparation of magnetic chitosan/Fe_2O_3 composite nanoparticles in tiny pools of water-in-oil microemulsion. React Funct Polym 66:1552–1558
8. Hritcu D, Popa MI, Popa N, Badescu V, Balan V (2009) Preparation and characterization of magnetic chitosan nanospheres. Turk J Chem 33:785–796
9. Li B, Jia D, Zhou Y, Hu Q, Cai W (2006) In situ hybridization to chitosan/magnetite nanocomposite induced by the magnetic field. J Magn Magn Mater 306:223–227
10. Li G-Y, Jiang Y-R, Huang K-L, Ding P, Chen J (2008) Preparation and properties of magnetic Fe_3O_4–chitosan nanoparticles. J Alloy Compd 466:451–456
11. Mürbe J, Rechtenbach A, Töpfer J (2008) Synthesis and physical characterization of magnetite nanoparticles for biomedical applications. Mater Chem Phys 110:426–433