

COMPOSITE MAGNETITE – CHITOSAN OBTAINED BY IN-SITU PROCEDURE

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Abstract. *A method for preparing magnetic crosslinked chitosan microparticles was developed. The chitosan encapsulated magnetite particles (Fe_3O_4) 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. The products were characterized regarding their size distribution (by laser diffraction analysis), morphology (TEM), composition (FTIR) and magnetic properties (magnetic susceptibility analysis). The synthesis parameters were optimized for obtaining colloidally stable magnetic microparticles bearing surface amino groups that can subsequently be used for complexing heavy metal ions. 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% magnetite content.*

Keywords: Magnetic particles, chitosan, magnetite, composite

1. Introduction

In recent years a lot of research efforts have been focused towards the application of magnetic particles in the field of wastewater treatment due to their response to magnetic force that provides facile separation after metal ion sorption using an external magnetic field [1]. Thus, an efficient, economic and eco-friendly separation of metal ions from wastewater can be achieved using surface modified Fe_3O_4 particles with polymers. The use of magnetite-chitosan composite material as a bio-adsorbent for wastewater appears to be a promising solution for metal ion removal. Various technologies for the removal of heavy metals from aqueous solutions have been utilized, such as ion exchange, chemical precipitation, reverse osmosis, membrane separation, nanofiltration and adsorption [2]. Chitosan magnetic composite particulate adsorbents provide multiple advantages, among which the facile separation from the aqueous phase [3,4], followed by regeneration and reuse [5]. Chitosan is a natural polysaccharide that consists of $\beta(1-4)$ 2-amino-deoxy-D-glucopyranose or N-acetyl-D- glucosamine residues and has

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an excellent adsorption behavior, mainly attributed to the presence of a large number of functional groups (primary amino and hydroxyl groups) that impart high chemical reactivity to the polymeric chain [6]. Yang and others have been summarized two methods for preparation of magnetic chitosan microspheres: reverse-phase suspension cross-linking method, and co-precipitation method [7]. The magnetite particles obtained in the initial step are subsequently covered with a layer of chitosan by ionotropic gelation [8] or based on the solubility of chitosan: it dissolves in acidic media and precipitates in alkaline conditions. New functional groups can be introduced by grafting in order to increase sorption selectivity for the target metal [9]. The magnetic chitosan grafted (alkyl acrylate) composites were prepared by radical copolymerization of butyl acrylate, butyl methacrylate or hexyl acrylate with ethylene glycol dimethacrylate onto the modified chitosan vinyl groups, with addition of magnetite nanoparticles in suspension [10]. An alternative, one step method for preparing chitosan-magnetite composites is described in this paper and it involves “in situ formation of magnetic chitosan particles” based on the oxidation of the ferrous ion within the polysaccharide matrix. The particle magnetization is varied by using certain chitosan/ ferrous chloride ratios.

2. Materials and methods

2.1 Reagents

Low molecular weight chitosan ($M_w = 50-190$ kDa; degree of deacetylation 84.5%), Pluronic F-127 and sodium hydroxide were obtained from Sigma-Aldrich (Sigma-Aldrich, Germany); ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), glutaraldehyde (25% solution in water) and potassium nitrate (KNO_3) were purchased from Merck (Merck, Germany); aqueous ammonia solution (25%[w/w]), glacial acetic acid (CH_3COOH) and hydrochloric acid 1N (HCl) were obtained from Chemical Company (Iasi, Romania). Unless otherwise stated, reagents have been used as purchased, without further purification. All solutions were prepared with bidistilled water

2.2. In situ preparation of chitosan- Fe_3O_4 particles

Magnetite/chitosan particles were obtained by in situ method. The magnetic materials are formed by mild oxidation of ferrous ion, entrapped in a chitosan-Fe(II) complex, using nitrate ion as a mild oxidizing agent, under alkaline conditions.

Briefly, chitosan was dissolved in 1M glacial acetic acid solution. This solution was transferred into an Erlenmeyer flask containing aqueous $FeCl_2 \cdot 4H_2O$ solution of various concentrations. The mixture was homogenized by ultrasonication under

reduced pressure for 15 minutes. The resulting chitosan-Fe complex was then precipitated in a three-necked round bottom flask placed in a water bath by the addition of aqueous ammonia solution, under mechanical stirring in nitrogen atmosphere. The resultant dark-green chitosan-Fe (OH)₂ complex was stirred for an hour in a water bath kept at 70°C. The mixture was then oxidized using aqueous 10% KNO₃ solution and aged under stirring for another hour at the same temperature. The obtained dark black particles were collected by sedimentation, washed with distilled water until neutral pH using magnetic field separation. The product was dispersed using Pluronic F-127 as a non-ionic surfactant and cross-linked with an aqueous glutaraldehyde solution under stirring and then washed with distilled water to remove the excess cross-linker. In order to remove the unreacted product, we performed an acid-base treatment followed by dialysis against distilled water

2.3. In situ synthesis of bare magnetite

Bare magnetite was obtained by the same method without the polysaccharide matrix. The results were compared with composite particles in terms of magnetization measurements.

2.4. Characterization

Particles size distribution was determined on laser diffraction analyzer (Shimadzu SALDI- 7001). The particle morphology was evaluated by microscopy (TEM) on dry sample. The magnetization was measured on a VSM 7410 vibrating sample magnetometer. Chemical composition was analyzed by FTIR (FTIR Bomem MB 104 spectrometer).

3. Results and discussion

3.1. Synthesis parameter study

The effect of the amount of ferrous chloride on the formation of composite microspheres was investigated. The synthesis parameters were optimized to yield the colloidally stable particles with uniform size distribution. Table 1 shows the variation of chitosan/ferrous ion ratio in the second column, the concentration of chitosan, ammonia and glutaraldehyde solution, but also the average volumetric (D_v) and numeric (D_n) particle size. The composite particles obtained by the optimum procedure had an average diameter of 40 μm with a 0.9/1 chitosan/Fe(II) ratio (Mag_IS_C3). Batch Mag_IS_C3, Mag_IS_C3_1 and Mag_IS_C3_2 are synthesized under the same conditions (optimum) and resulted in particles with

comparable size (between 39 and 45 μm), proving that the procedure is reproducible.

Table 1. Synthesis parameter study

Batch	CS/Fe(II) ratio, g/g	CS conc, %	Ammonia solution conc, M	GLA conc, %	Dv, μm	Dn, μm
Mag IS C1	0.9/0.3	3	0.5	5	60	41
Mag IS C3	0.9/1	3	0.5	5	40	21
Mag IS C2	0.9/2	3	0.5	5	67	48
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

Overlay size distribution curves for batches Mag_IS_C1, C2 and C3 are shown in Fig.1. The results prove that batch Mag_IS_C3 presents the most uniform distribution in the laser diffraction measurements.

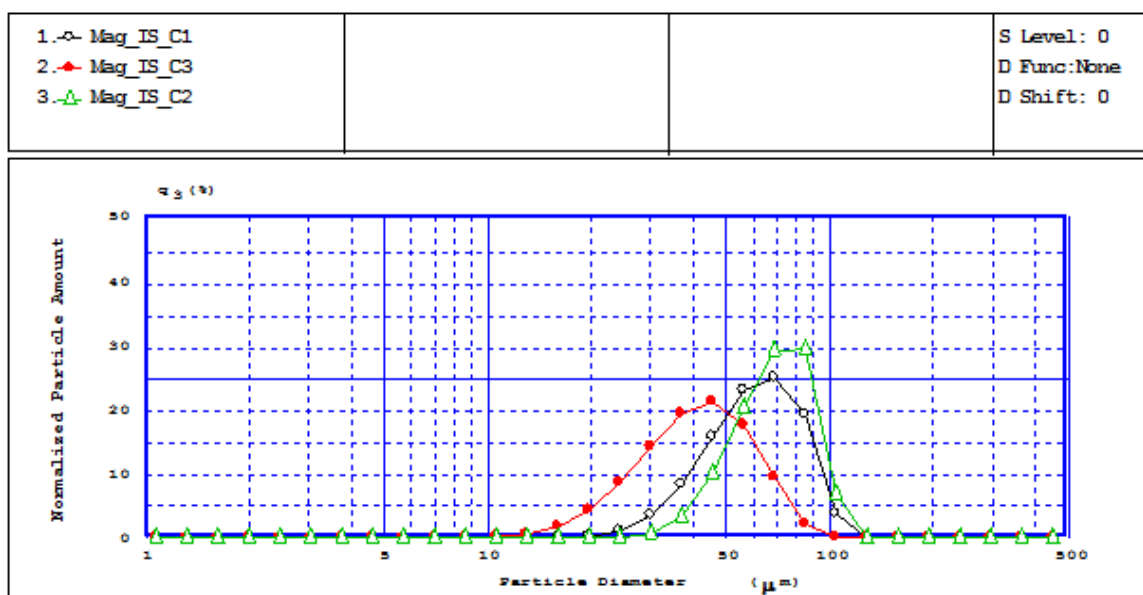


Fig. 1. Particle size distribution of composite particles

3.2. FTIR analysis

Overlay IR spectra of raw chitosan (CS_LMW), bare magnetite (Mag_P) and composite particles (batch Mag_Is_C3) are shown in Fig. 2.

The peak located in the 576 cm^{-1} region, characteristic for the Fe-O group is found in bare magnetite and composite particles spectra, confirming that the product

contains magnetite. In the Mag_IS_C3 spectrum its appearance is slightly modified, probably due to attachment to the polymeric matrix. The peak around 1637 cm^{-1} , assigned to the N-H group bending vibration, is present both in raw chitosan and in the composite material spectra, proving that magnetite particles were successfully encapsulated into the chitosan matrix.

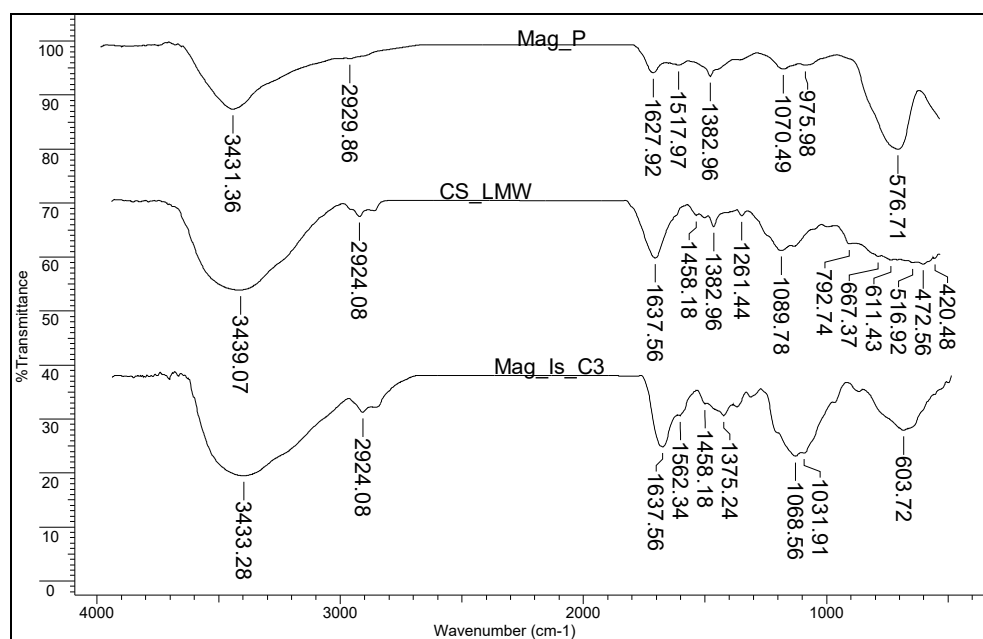


Fig. 2. IR spectra bare magnetite (Mag_P), chitosan (CS_LMW) and composite particles (in Mag_IS_C3)

3.3. Microscopy

The particle morphology was analyzed by TEM (composite particles, batch Mag_IS_C3) and the images are presented in the Figure 3. The picture shows that the magnetite is encapsulated into the polysaccharide matrix. The detail at higher magnification confirms that the magnetite particles remain distinct. The lack of agglomeration phenomena (which would result in mutual magnetization cancellation) explains the high magnetization of the resulting composite.

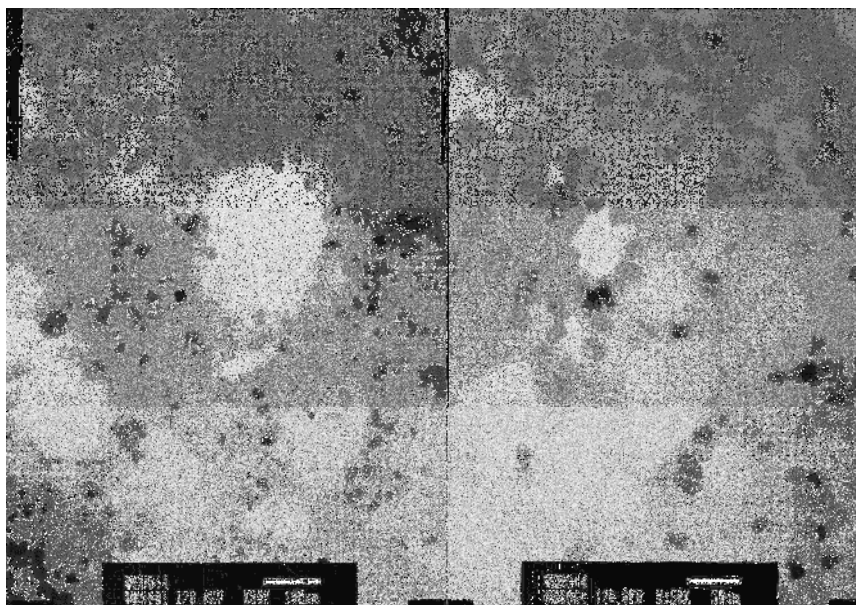


Fig. 3. TEM images of composite particles (batch in Mag_IS_C3)

3.4. Magnetization measurements

The magnetization curves obtained for bare magnetite and composite particles with different ratios chitosan/ferrous ion are presented in figure 4. The magnetic saturation was 51.07 emu/g for bare magnetite and 24 emu/g for the chitosan/magnetite particles (Mag_Is_C3) obtained by the optimum procedure, corresponding to about 47% magnetite content. The results show an increase in magnetization at higher chitosan/ferrous ion ratio, proving the versatility of the synthesis method. Table 2 presents the magnetite content for each batch according to the varied ratios.

Table 2. Magnetite content determined from the magnetization curves

Batch	Magnetite content, %
Mag IS C1	31.3%
Mag IS C3	47.05%
Mag IS C2	82.3%

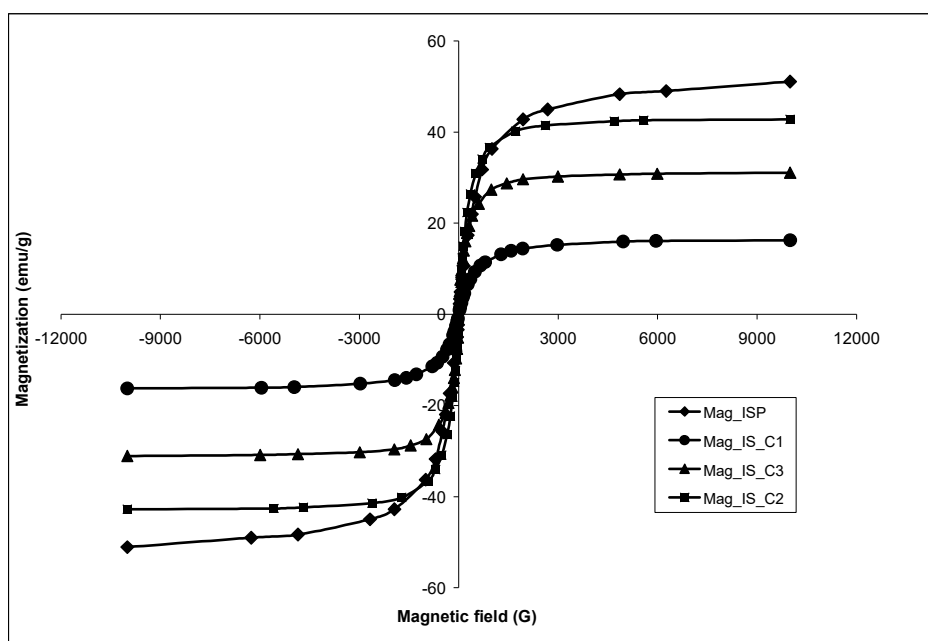


Fig. 4. Magnetization measurements of particles obtained with various chitosan/iron chloride ratios compared with bare magnetite

Conclusions

A simple method for preparing magnetite/chitosan composite microparticles using in situ procedure is described. The particles were characterized with respect to their morphology, size and magnetic behavior. The magnetization measurements confirm the presence of variable amounts of magnetite uniformly dispersed within the polymeric matrix according to the varied ratios. Due to the presence of amine sites on the surface of magnetite/chitosan microparticles, that are well-known reactive groups for metal ion complexation, the product can be used for removal of heavy metals from wastewater.

REFERENCES

1. Webster A, Halling M. D., Grant D. M., (2007), Metal complexation of chitosan and its glutaraldehyde cross-linked derivative, *Carbohydrate Research*, **342**, p. 1189–1201
2. Barakat, M.A., (2011) New trends in removing heavy metals from industrial wastewater: review article, *Arabian Journal of Chemistry*, **4**, p. 361–377

3. Kyzas, G.Z., Kostoglou, M., (2015), Swelling–adsorption interactions during mercury and nickel ions removal by chitosan derivatives. *Separation Purification Technology*, **149**, p. 92–102
 4. Podzus, P.E., Daraio, M.E., Jacobo, S.E., (2009) Chitosan magnetic microspheres for technological applications: preparation and characterization, *Physica B*, **404**, p. 2710–2712
 5. Ge, F., Li, M.M., Ye, H., Zhao, B.X., (2012), Effective removal of heavy metal ions Cd^{2+} , Zn^{2+} , Pb^{2+} , Cu^{2+} from aqueous solution by polymer-modified magnetic nanoparticles. *Journal Hazardous Materials*, **211–212**, p. 366–372
 6. Crini G., (2005), Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, *Progress Polymer Science*, **30**, p. 38–70
 7. Yang Hu, Yuan Bo, Yao Bo Lu, Rong Shi Cheng, (2009), Preparation of magnetic chitosan microspheres and its applications in wastewater treatment, *Science China Serie B-Chemistry*, **52**, p. 249-256
 8. Hritcu D., Popa M. I., Popa N., Badescu V., Balan V., (2009), Preparation and characterization of magnetic chitosan nanospheres, *Turkish Journal of Chemistry*, **33**, p. 785-796
 9. Donia A. M., Atia A. A., Elwakeel K. Z, (2007), Recovery of gold(III) and silver(I) on a chemically modified chitosan with magnetic properties, *Hydrometallurgy*, **87**, p. 197–206
 10. Iordache M.L., Dodi G., Hritcu D., Draganescu D., Chiscan O., Popa M. I., (2018), Magnetic chitosan grafted (alkyl acrylate) composite particles: Synthesis, characterization and evaluation as adsorbents, *Arabian Journal of Chemistry*, **11**, p. 1032–1043
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