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Preparation and characterization of magnetic nanoparticles with chitosan coating

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Abstract. Magnetic chitosan nanoparticles were prepared by the suspension cross-linking technique for use in the application of magnetic carrier technology. The Fe₃O₄ magnetic nanoparticles were synthesized by co-precipitation of FeCl₂ and FeCl₃ solution in base medium for using in the preparation of the magnetic chitosan. The morphological and magnetic properties of the magnetic nanoparticles were characterized by different techniques (TEM, XRD, VSM, FTIR, etc.). The magnetic properties of chitosan – magnetic nanoparticles were analyzed by VSM, and Mₛ around 15 emu/g.

Keyword: Magnetic nanoparticles, chitosan.

1. Introduction

The recent developments of nanotechnology in synthesizing biocompatible and functionalized magnetic nanoparticles have numerous novel applications in biomedicine as well as diagnosis [1-7]. Especially, Fe₃O₄ ferrites magnetic nanoparticles have been rising as a significant useful material due to their specific properties such as superparamagnetic, non toxic and small size, etc. Magnetic nanoparticles are used to coat several surfactants to anti – aggregation which was caused by magnetic dipole – dipole attractions between particles [1, 2, 7]. The studies of utilizing various biocompatible and biodegradable polymers which can functionalize and modify the surface of the Fe₃O₄ nanoparticles have been broadly developed [2, 6, 7]. A magnetic nanoparticle is usually composed of the magnetic cores and a polymeric shell having favorable functional groups and features for various applications [8, 9].

Magnetic nanoparticles technology is a significant method for solving decomposition, inactivation or deformation in biochemical processes such as separation, purification, etc. In this technology, magnetic particles are used as the support materials and they can be easily separated from the reaction medium and stabilized in a fluidized reactor by applying a magnetic field [1, 2, 7, 9]. The most popular applications of magnetic carrier technology are bioaffinity chromatography, wastewater treatment, immobilization of enzymes or other biomolecules and the preparation of immunological assays [9].

Chitosan, a partially acetylated glucosamine, poly(1 → 4)-2-amino-2-deoxy-d-glucan, biopolymer which exist in cell walls of some fungi such as the Mucorales, is a polyaminosaccharide with many
significant biological (biodegradable, biocompatible and bioactive) and chemical properties (polycationic, hydrogel, reactive groups such as OH and NH$_2$) [1, 2, 7, 9]. Therefore, it is used in many different types of applications (i.e. wastewater treatment, chromatographic support, enzyme immobilization, drug-delivery systems). Chitosan can be produced by alkaline deacetylation of chitin, and chitin is the second most abundant natural polymer after cellulose, and therefore is a very cheap biopolymer [9].

In this study, we prepared magnetic Fe$_3$O$_4$-chitosan nanoparticles by coprecipitation Fe(II) and Fe(III) in the presence of ammonium. And then, the suspension cross-linking technique was used for the preparation of magnetic chitosan nanoparticles and glutaraldehyde was used as a cross-linker. The size and the size distribution, magnetic properties and the functional groups of the magnetic chitosan microspheres were evaluated using selected parameters (such as stirring rate of the suspension medium, molecular weight of the chitosan and the Fe$_3$O$_4$/chitosan ratio).

The structure, size and the size distribution, magnetic properties and functional groups of magnetic nanoparticles were evaluated using of a Vibrating Sample Magnetometer (VSM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), Fourier Transforms Infrared (FTIR) spectroscopy.

The magnetic-chitosan nanoparticles in this study were applied in the immobilizing enzyme in biotechnology or removal of heavy metal ions in environment at technology.

2. Experimental

2.1. Materials
Chitosan polymer 150 kDa was obtained from Fluka (Switzerland). Aqueous acetic acid (Aldrich, USA) solution was used as a solvent for the chitosan polymers and glutaraldehyde (Merck, Germany) was used as the cross-linker. The suspension medium was composed of a mixture of paraffin (Merck, Germany), and Span-80 (Merck, Germany) was added as an emulsifier. All chemicals were of analytical grade and no further purification was required.

2.2. Preparation of magnetic nanoparticles
Fe$_3$O$_4$ nanoparticles were prepared by coprecipitation method with a ferrous complex in presence of NH$_4$OH. Firstly, FeCl$_2$.4H$_2$O and FeCl$_3$.6H$_2$O [Fe$^{2+}$: Fe$^{3+}$= 1:2] were dissolved in about 50 ml re-dionized water, and stirring this solution under strong ultrasonic agitation while heating solution to 70°C. Next, this iron solution source was added drop-wise into NH$_4$OH under strong ultrasonic agitation for 30 minutes, and bubbling N$_2$ gas.

The chemical reaction of Fe$_3$O$_4$ precipitation is expected as follows:

$$\text{FeCl}_2.4\text{H}_2\text{O} + 2\text{FeCl}_3.6\text{H}_2\text{O} + 8\text{NaOH} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NaCl} + 20\text{H}_2\text{O}$$

Black Fe$_3$O$_4$ particles were decanted by permanent magnet and cleaned by re-dionized water several times.

2.3. Preparation of magnetic chitosan nanoparticles
The suspension cross-linking technique was used for the preparation of magnetic chitosan nanoparticles. In this specific procedure, a 5% chitosan solution was prepared using a 2% aqueous acetic acid solution containing 0.2 g Fe$_3$O$_4$ dry magnetic nanoparticles. And then, this solution was poured, drop-wise, into the dispersion medium, which was composed of 30 ml paraffin and 0.5 ml span-80. During this process, the dispersion medium was stirred with a strong ultrasonic agitation at room temperature. Next, an additional 3 ml 25% glutaraldehyde solution was added to the dispersion medium and then solution was stirred for further 5 h. At the end of this period, the chitosan-magnetite nanocomposite particles were recovered from the reaction mixture by using a permanent magnet; the products were washed with ethanol and dried in a vacuum oven at 500°C for 2 days.
3. Results and discussions

3.1. Synthesis of Fe₃O₄ nanoparticles with chitosan coating
The preparation of magnetic chitosan nanoparticles proceeds in two steps by cross-linking methods as follows:
- The synthesis of Fe₃O₄ particles by coprecipitation of equimolar Fe(III) and Fe(II) in the presence of NH₄OH. Schematic representation of the preparation of Fe₃O₄ nanoparticles was shown in equation (1).
- Chitosan and Fe₃O₄ were mixed in appropriate proportion to form the chitosan-magnetite nanocomposite particles with amine group by reverse-phase suspension cross-linking method.

3.2. Particle size and structure of Fe₃O₄–chitosan nanoparticles
The morphology of naked and Fe₃O₄ with chitosan coating were shown in figure 1. The magnetic particles showed a small size in nanoscale before and after being coated by chitosan. The image of Fe₃O₄ nanoparticles, was shown in figure 1, was proved that Fe₃O₄ particles were monodisperse and had a mean diameter of 15-17 nm. The TEM image of Fe₃O₄–chitosan nanoparticles in figure 2b was showed that the structure of CTS-coated magnetite nanoparticles was looser, causing to the increasing in size, the average diameter of such a structure was 23-25 nm.

This also represented that the coating process did not significantly effect the agglomeration and the change in size of the particles. However, the aggregative phenomenon still present a little in the Fe₃O₄–chitosan nanoparticles.

3.3. Phase structure of Fe₃O₄ magnetic nanoparticles
The XRD patterns for the naked and Fe₃O₄ nanoparticles coated with chitosan were showed in figure 3. Six characteristic peaks for Fe₃O₄ marked by their indices (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) were observed for both samples reveal that the resultant nanoparticles were pure Fe₃O₄ with inverse-spinel structure.

That is the reason for the unchangeable pace of Fe₃O₄ during coating process. In the pattern of XRD diffraction, the broad nature of the diffraction bands indicated that Fe₃O₄ have small particle sizes. The particle sizes can also be quantitatively evaluated from the XRD data using the Debye–Scherrer equation which gives a relationship between peak broadening in XRD and particle size:

\[ d = \left( \frac{k\lambda}{\beta \cos \theta} \right)^{\frac{1}{2}} \]
where \( d \) is the particles size, \( k \) is the Debye–Scherrer constant (0.89), \( \lambda \) is the X-ray wavelength (0.15406 nm) and \( \beta \) is the full width at half maximum, \( \theta \) is the Bragg angle. According to the Debye-Scherrer equation (2), the particles size of the naked and the chitosan coated Fe\( _3 \)O\( _4 \) nanoparticles is 15 and 23 nm, respectively.

3.4. FTIR spectra analysis

Figure 3 shows FTIR spectra of naked Fe\( _3 \)O\( _4 \), chitosan (CTS), and Fe\( _3 \)O\( _4 \)-chitosan nanoparticles (CF1) and we can affirm the binding between the other groups. The peak around 3440 cm\(^{-1}\) observed in curve CTS and magnetic CTF1 indicates to the OH group. The peak at 543 cm\(^{-1}\) relates to Fe–O bond. In the IR spectrum of CTS, the characteristic absorption bands appeared at 1570 cm\(^{-1}\) which can be assigned to N–H bending vibration, peaks 1309 cm\(^{-1}\) appeared to C–O stretching of primary alcoholic group in chitosan.

In the spectrum of Fe\( _3 \)O\( _4 \)-chitosan nanoparticles (figure 3), compared with the spectrum of CTS, the 1570 cm\(^{-1}\) peak of N–H bending vibration shifted to 1558 cm\(^{-1}\), and a new sharp peak 1627 cm\(^{-1}\) appears, it indicated that chitosan react with glutaraldehyde to form the Schiff base, and a new sharp peak 577 cm\(^{-1}\) relates to Fe–O bond appears. Results indicated that CTS was coated to the magnetic Fe\( _3 \)O\( _4 \) nanoparticles successfully. Because the surface of iron oxide with negative charges has an affinity toward CTS, protonated CTS could coat the magnetite nanoparticles by the electrostatic interaction and chemical reaction through glutaraldehyde cross-linking.
3.5. Magnetic properties of magnetic nanoparticles

Magnetic materials having around a dozen nanometers in size are used to show a superparamagnetic behavior in which coercivity and remanence has zero value. The hysteresis loop of magnetic Fe$_3$O$_4$ nanoparticles naked and coated with chitosan at room temperature is showed in figure 4. As could be seen no remanance and coercivity is observed in the magnetic loop. This phenomenon proved that magnetic nanoparticles made from this study are superparamagnetic. Also in figure 4, saturated magnetization M$_S$ of pure magnetic nanoparticles is 70 emu/g while of magnetic chitosan coating is 15 emu/g. This represented that magnetic properties of particles after coating have a content of 25% by comparing the value of naked particles.

The remanence of span-80 on the surface of magnetic nanoparticle could be due to the loss of magnetic properties of magnetic chitosan nanoparticles because it caused a magnetically dead layer. Because any crystalline disorder existed in the surface layer could also cause a significant decrease of saturated magnetization. Ferrite magnetic nanoparticle with special properties- superparamagnetic is an especially important material for applying to magnetic targeting carriers.

4. Conclusions

The magnetic Fe$_3$O$_4$-chitosan nanoparticles were synthesized by binding chitosan on the surface of Fe$_3$O$_4$ nanoparticles. The results from TEM and XRD proved that the Fe$_3$O$_4$-chitosan nanoparticles were inverse- spinel structure, monodisperse and quite sphere in shape with a mean diameter of 23 nm. The coating process had no changing effect in the spinel structure of Fe$_3$O$_4$. The saturated magnetization of magnetic chitosan nanoparticles could reach 15 emu.g$^{-1}$ and the nanoparticles showed the characteristics of superparamagnetism. The nanoparticles have a potential for use in assisted drug delivery systems, cell/enzyme immobilization and many other industrial processes.

References