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Research Article

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Sonochemical Preparation of α-Fe_2O_3 Nanoparticles in a Dual Biopolymer Matrix

Selcan Karakus*, Merve Ilgar, Ezgi Tan, Ayben Kilislioglu

Department of Chemistry, Faculty of Engineering, Istanbul University-Cerrahpasa, Istanbul, Turkey

***Corresponding author:** Selcan Karakus, Department of Chemistry, Faculty of Engineering, Istanbul University-Cerrahpasa, 34320 Avcilar, Istanbul, Turkey. Tel: +90-2124737000; Fax: +90-2124737180; Email: selcan@istanbul.edu.tr

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Abstract

The present study relates to a biodegradable antibacterial bio-nanocomposite made of biopolymers carboxy-methyl cellulose and chitosan. Dual biopolymer matrix was preferred to enhance stability and dispersion of α-Fe_2O_3 nanoparticles. The biopolymer matrix was synthesized by solution method without introducing any other poisonous cross-linking agents. α-Fe_2O_3 nanoparticles were synthesized in chitosan after reduction of Fe (III) ions with sodium borohydride and then dispersed into chitosan/carboxy-methyl cellulose@Sepiolite and chitosan/carboxy-methyl cellulose@Silica. Viscosity behavior, thermal properties and antibacterial activity of the bio-nanocomposite were evaluated. Experimental results show that the thermal stability of the composite material reinforced because of the well dispersion of α-Fe_2O_3 nanoparticles were into the biopolymer matrix. Dispersion and size of Hematite (α-Fe_2O_3) nanoparticles was determined by X-ray diffraction and scanning electron microscopy analysis. Antibacterial activity of bio-nanocomposites was tested by comparing mean diameter of inhibition zone against gram negative bacteria. The bio-nanocomposite was tested for antimicrobial activities against pathogenic bacteria like *Escherichia coli* (gram negative bacteria). The bio-nanocomposite can be used as a preservative additive in environments where bacteria are not desired.

Keywords: Antibacterial; Bio-Nanocomposite; Carboxy-Methyl Cellulose; Chitosan; α-Fe_2O_3

Introduction

Nanotechnology is a new multidisciplinary area with developed physical, optical, electrical, barrier and chemical properties in the nanoscale (1-100 nm). Two different approaches (top-down approach and bottom-up) are used for the production of nanomaterials [1]. Two approaches are used for the production of nanomaterials [2]. Laser ablation, dispersion, high vacuum evaporation and electrochemical reduction are supported top-down approaches [3]. The assembling of atoms or clusters to prepare nanoparticles is known bottom-up approach [4]. The stability, size, morphology, and other properties of nanomaterials are influenced by their physical conditions, the structure of the reducing agents and the stabilizing agents [5]. The production of nanomaterials is divided into three categories: physical, chemical and biological methods [6]. Different physical methods are used for the fabrication of nanomaterials such as spray deposition, laser ablation or cluster beam deposition, microwave, evaporation-condensation, sonochemical and milling [7]. The sonochemical method is known as a low cost and efficient method for the synthesis of nanomaterials. The sonochemical process creates acoustic bubbles in an aqueous medium. The micro bubbles form during acoustic cavitation tend to increase or decrease their size until they reach their resonance size. It is the mean size of the bubble before undergoing the violent explosion. After explosion the bubbles produce very high heat, pressure and various free radicals. The bubbles are known center for the chemical reaction and related to micro-reactors or hot spots. The acoustic cavitation light is emitted due to the bubbles collapse and depends on the intensity and frequency of ultrasonic waves. [8,9]. The ultrasonic effect allows the conversion of macrostructured materials into nanostructures rapidly by the acoustic cavitation under unusual

reaction conditions at high-pressure, high-temperature and high energy profiles (5000 K and 1000 atm) [10].

Different polymers, such as alginate [11], Polyethylene Glycol (PEG) [12], poly (lactic-acid) (PLA) [13], poly (vinyl alcohol) (PVA) [14], cellulose [15] and chitosan [16] are selected for the polymer matrix of nanomaterials. Biopolymers are suitable chemicals as nanostructures for biomedical applications due to their biocompatibility, biodegradability and low immunogenicity properties. Biopolymer-based nanoparticles are preferred as drug/gene delivery carriers and antibacterial agents [17].

In this study, we focused on Carboxy-Methyl Cellulose (CMC) and chitosan and dual biopolymer matrix. Carboxy-Methyl Cellulose (CMC) is one of the important cellulose derivatives, possesses many desirable properties, such as good filming, water maintaining, bind and emulsification. CMC can play an important role as a blend polymer to increase the hydrophilicity [18]. Chitosan (Chi), which is generally obtained by deacetylation of chitin, is a natural cationic polysaccharide. It has biocompatibility, biodegradability and antibacterial activity [19]. CMC and chitosan were used as a polymer matrix in producing the new nanostructure with an antibacterial characteristic. In order to enhance its surface properties a small amount of inorganic additive (silica or sepiolite) was added and homogeneously dispersed through the matrix by using sonochemical method. The antibacterial properties of the nanostructure were investigated by the addition of α-Fe_2O_3 nanoparticles by comparing mean diameter of inhibition zone against gram negative bacteria Escherichia coli.

Materials and Methods

Materials

Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) (≥99%), Chitosan (low molecular weight), Carboxy-Methyl Cellulose (CMC) (high viscosity) were purchased from Sigma-Aldrich. Sodium borohydride ($NaBH_4$) ≥ 98,0 % (m), ethyl alcohol (C_2H_5OH) (absolute for analysis EMSURE® ACS, ISO, Reag. Ph Eur), silica gel SiO_2 (Si) (high-purity grade, pore size 60 Å, 70-230 mesh) were purchased from Merck. Sepiolite (Sep) was provided from Eskisehir (Turkey).

Methods

Chi/CMC@ α-Fe_2O_3 - Si bionanocomposite was prepared in four steps:

- Iron (III) chloride solution was prepared by dissolving 0.54 g $FeCl_3 \cdot 6H_2O$ in 24 mL ethanol / 6 mL distilled water mixture. 0.1 M $NaBH_4$ solution was added to iron (III) chloride solution drop by drop and solution was stirred vigorously under nitrogen gas atmosphere.
- 0.1 g CMC was dissolved in 100 mL water for 24 h and 0.05 g Chitosan was dissolved in 50 mL 2% glacial acetic solution for 30 min. All polymer solutions were mixed.
- 0.02 g silica was dispersed in 100 mL water.
- The silica and iron solutions were mixed under constant stirring. Finally, the iron solution was added to the polymer mixtures under sonicator for 10 min. After doing homogenization, the homogenized solution was dried onto a petri plate and dried at 80°C (Figure 1).

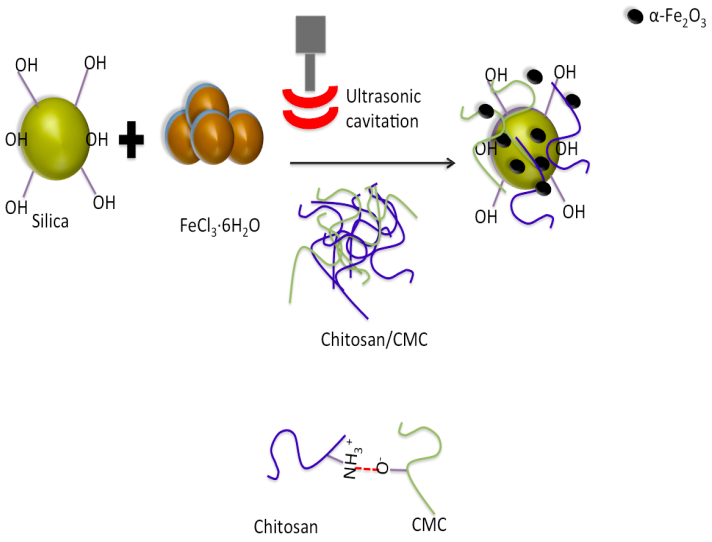

Figure 1: Preparation of Chi/CMC@ α-Fe_2O_3 -Si bionanocomposite.

Synthesis of Chi/CMC@ α-Fe_2O_3 -Sep bio-nanocomposite

Chi/CMC@ α-Fe_2O_3 -Sep bionanocomposite was prepared in three steps:

- Iron (III) chloride solution was prepared by dissolving 0.54 g $FeCl_3 \cdot 6H_2O$ in 24 mL ethanol / 6 mL distilled water mixture. 0.1 M $NaBH_4$ solution was added to iron (III) chloride solution drop by drop and solution was stirred vigorously under nitrogen gas atmosphere.
- 0.1 g CMC was dissolved in 100 mL water for 24 h and 0.05 g Chitosan was dissolved in 50 mL 2% glacial acetic solution for 30 min. All polymer solutions were mixed.
- 0.02 g sepiolite (Eskisehir, Turkey) was dispersed in 100 mL water.
- The sepiolite and iron solutions were mixed under constant stirring. Finally, the iron solution was added to the polymer mixtures under sonicator for 10 min. After doing homogenization, the homogenized solution was dried onto a petri plate and dried at 80°C (Figure 2).

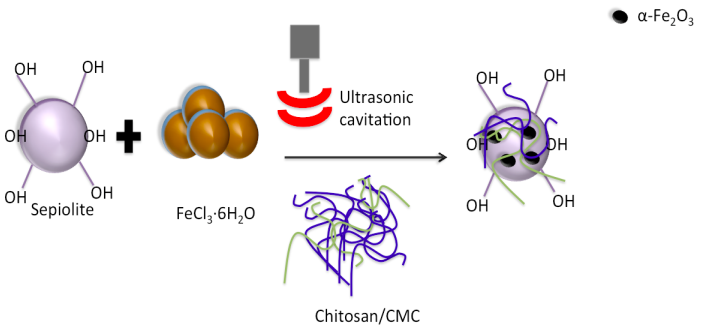

Figure 2: Preparation of Chi/CMC@ α-Fe_2O_3 -Sep bionanocomposite.

Characterization

The surface morphology of nanostructure was investigated using a Scanning Electron Microscope (SEM, Quanta FEG 450). An X-ray diffractometer (Bruker D8 Advance X-ray Diffractometer) was used with CuKα (λ =0.15418 nm, 40 kV, 40 mA) radiation over a range of 2θ angles from 2 to 75, with a step size of 0.02˚/s. FTIR spectroscopy was recorded using the Perkin Elmer FTIR emission spectrometer (Spectrum Two) and nanostructures were properly ground with KBr powder and were analyzed from 4000 to 600 cm^{-1} frequency range with a resolution of 4 cm^{-1} and 8 scans. Thermal gravimetric analysis (TGA, Shimadzu TGA-50) was used to determine thermal characteristics of bio-nanocomposite to determine degradation temperatures and absorbed moisture content. (12.4 mg sample was heated at a rate of 10˚C/min at 25˚C-1000˚C under nitrogen atmosphere. Viscosity measurements were performed in a AND viscometer at 25±0.5˚C (Figure 3)). Viscosity measurements accuracy is ±10.0%±1 digit of indicated value and reproducibility is 0.2%.

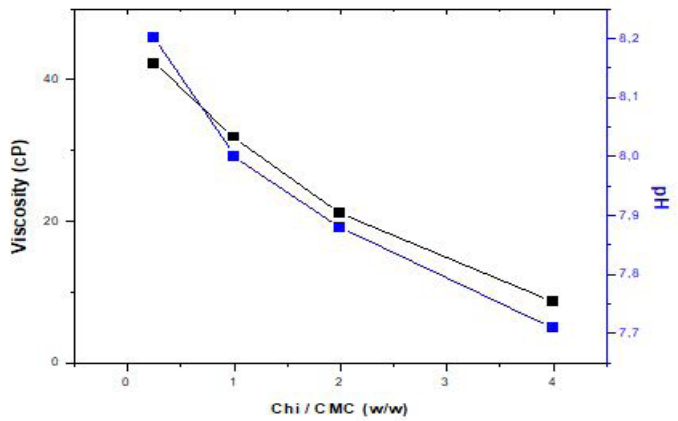

Figure 3: Physical parameters of dual polymer.

Results and Discussion

Morphology and Structure

SEM Analysis: In order to evaluate the dispersion of α-Fe_2O_3@ silica in Chitosan/CMC dual polymer matrix morphological studies was performed with scanning electron microscopy (FEG Quanta FEG 450 version FE-SEM microscope, operating at an accelerating voltage of 20 kV). The sample was coated with a ca. 5 nm gold layer prior to measurement a SEM micrograph of the Chi/CMC@α-Fe_2O_3-Si bio-nanocomposite is shown in (Figure 4). SEM images of the nanostructures revealed that the Chi/CMC@α-Fe_2O_3-Si bio-nanocomposite had a relative good dispersion of the α-Fe_2O_3@silica nanoparticles of sizes in the range of 150-200 nm and a good contact between them and the dual biopolymer matrix was also observed.

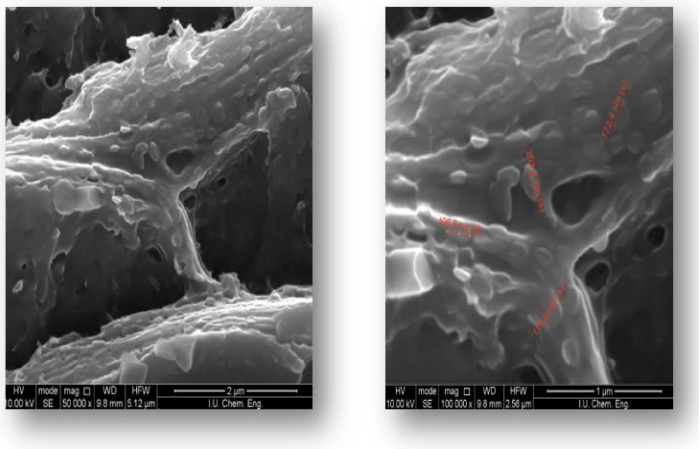

Figure 4: SEM micrographs of the Chi/CMC@α-Fe_2O_3-Si bio-nanocomposite.

XRD Analysis: X-ray powder Diffraction (XRD) was used to identify the structural properties of nanostructures and to determine the crystallinity of the samples. The powder XRD patterns of α-Fe_2O_3 based samples are shown in (Figure 5). Diffraction peaks (2θ: 31˚, 45˚) were observed at corresponding to hematite with lattice parameters of 24 nm [20]. The crystallite sizes of samples were calculated by using the Debye-Scherrer formula [21].

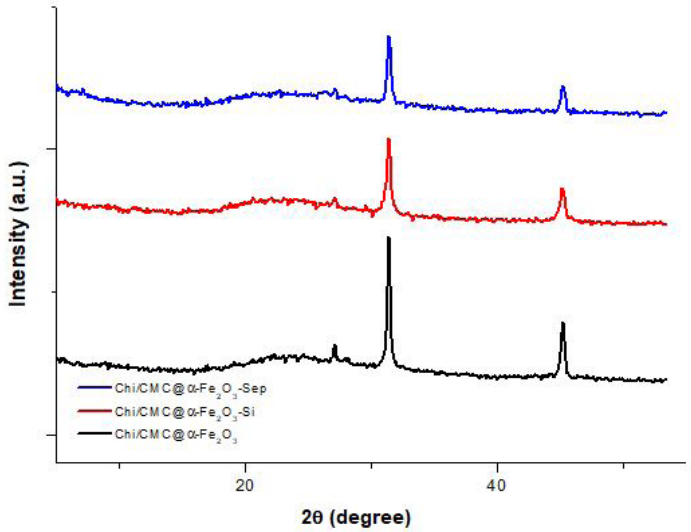

Figure 5: XRD analysis of the bio-nanocomposites.

Thermal Properties

Thermogravimetric (TGA) curves of the samples are shown in (Figure 6). The curves show that the process of weight loss takes place in four main steps. The TGA data of bio-nanocomposites have four successive steps of decomposition. It is described [22] that exist three different types of water depending of the chemical structure: free water at about 40-60˚C, water linked through hydrogen bonds at 80-120˚C, and released water at 160˚C. The total estimated mass loss of 50% at 150-1000˚C with a complete decomposition is observed for CO, CO_2, NO, NO_2, etc. gases.

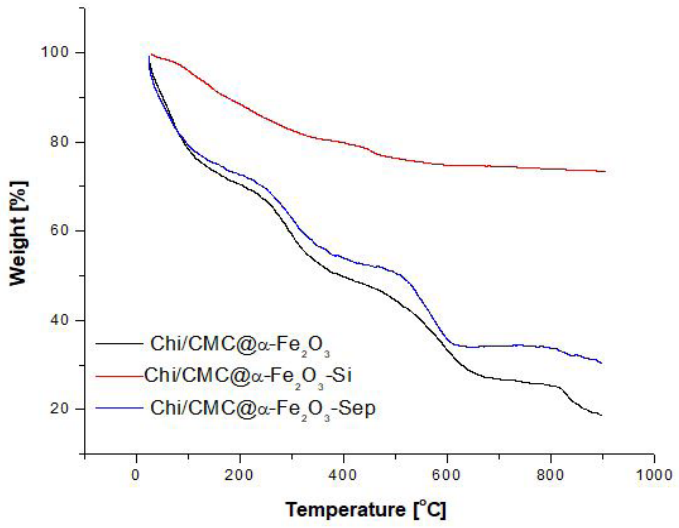

Figure 6: TGA thermogram of a) Chi/CMC@α-Fe_2O_3, b) Chi/CMC@α-Fe_2O_3-Si and c) Chi/CMC@α-Fe_2O_3-Sep.

FTIR Analysis: The FTIR spectra of the bio nanocomposites are shown in (Figure 3). The interactions between polymer matrix and inorganic additive were studied by FTIR analysis (Figure 7). In FTIR spectra, all the characteristic peaks of Chi and CMC were observed at 3479 cm^{-1} (-OH), at 2924 cm^{-1} (-OH), at 1750 cm^{-1} (C=O stretching), at 1514 cm^{-1} (-NH) and at 1318 cm^{-1} (-CH_2OH) peaks. FTIR spectrum of samples were found a very intense band below 530 cm^{-1} related to α-Fe_2O_3.

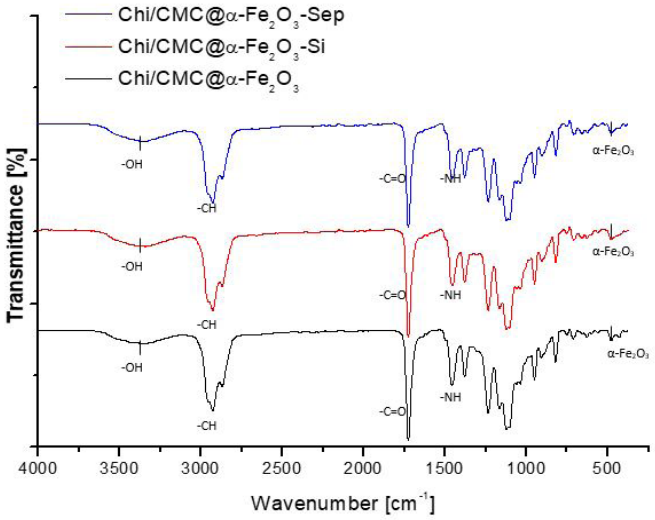

Figure 7: Infrared spectroscopy (ATR-IR) data of a) Chi/CMC@α-Fe_2O_3, b) Chi/CMC@α-Fe_2O_3-Si and c) Chi/CMC@α-Fe_2O_3-Sep.

According to FTIR spectrum the driving forces between the inorganic and organic phase are non-covalent interactions. The penetration of inorganic additive between the dual polymer matrix occurred by intercalation. Based on these results, this nanostructure resulting from interactions such as electrostatic, hydrogen bonds, van der Waals was obtained by sonochemical effect.

Antibacterial activity: Antibacterial metal nanoparticles were found more stable particularly at high temperatures and/or pressures in literature [23]. This work was focused on the antibacterial behaviour of α-Fe_2O_3 nanoparticles with silica or sepiolite in dual polymer matrix (Chi/CMC@α-Fe_2O_3-Sep and Chi/CMC@α-Fe_2O_3-Si bio-nanocomposite). The antibacterial assay results were investigated the antibacterial activity of α-Fe_2O_3 nanoparticles against *Escherichia coli* (gram negative bacteria) and evaluated by a modified Kirby Bauer method. After 24 h incubation at 37˚C, the Chi/CMC@α-Fe_2O_3-Si bio-nanocomposite clearly showed antibacterial property against Gram Negative *E. coli* (Figure 8) (the zones of inhibition ~ 15 mm). However, no significant inhibition zone was found in the Chi/CMC@α-Fe_2O_3-Sep. These experimental results showed that the antibacterial activity was became effective with the α-Fe_2O_3 based silica whereas it wasn't demonstrated with sepiolite. According to the experimental results, one could emphasize that the antibacterial activity was depended on the addition of silica and role of its surface.

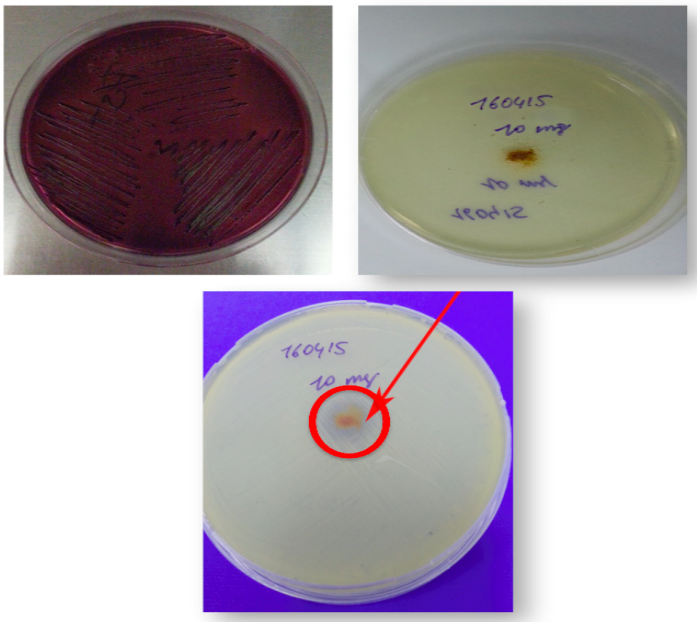

Figure 8: Antibacterial analysis of Chi/CMC@α-Fe_2O_3-Si bio-nanocomposite.

Conclusion

α-Fe_2O_3 nanoparticles were synthesized and dispersed into the dual biopolymer matrix which is consist of chitosan and CMC by sonochemical method. The characterization of the nanostructure was done by Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) techniques.

- XRD results and the SEM images showed the homogeneous silica dispersion into the dual polymer matrix. The aggregation of SiO_2 did not occur. Results showed that SiO_2 can be used as nanofiller without any surface functionalization.
- Thermogravimetric analysis of Chi/CMC@α-Fe_2O_3-Si bio-nanocomposite were studied as a function of percentage weight loss with temperature.
- The antibacterial activity is examined against the Gram-negative *Escherichia coli*. The antibacterial activity of the new material is largely dependent both on the size and the dispersion of α-Fe_2O_3 based silica particles.

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