Inclusion complexes of β-cyclodextrine with Fe_3O_4@HA@Ag
Part I: Preparation and characterization

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REZUMAT – ABSTRACT

Complecși de incluziune ai β-ciclodextrinei cu Fe_3O_4@HA@Ag
Partea I: Preparare și caracterizare

În acest studiu, a fost abordată prepararea complecșilor de incluziune în conformitate cu tehnicile de malaxare și amestecare fizică la 1:1 și 1:2 (oaspete:gazdă), raportul de masă al Fe_3O_4@HA@Ag și β-ciclodextrinei. S-au efectuat: spectroscopia în infraroșu cu transformata Fourier, analizele termogravimetrice și analizele de microscopie electronică cu scanare ale complecșilor preparați. Conform rezultatelor obținute, s-a observat că Fe_3O_4@HA@Ag formează în mod special complexul de incluziune cu β-ciclodextrina la un raport de masă de 1:2. În cea de-a doua parte a acestui studiu, sunt expuse rezultatele legate de utilizarea acestor complecși de incluziune în timpul procesului de electrofilare pentru a obține nanovăluri de fibre antibacteriene, care ar putea fi utilizate în cazul rănilor.

Cuvinte-cheie: β-ciclodextrină, complex de incluziune, Fe_3O_4@HA@Ag, microscop electronic cu scanare

Inclusion complexes of β-cyclodextrine with Fe_3O_4@HA@Ag
Part I: Preparation and characterization

In this study, the preparation of inclusion complexes according to kneading and physical mixing techniques at 1:1 and 1:2 (guest:host) mass ratios of Fe_3O_4@HA@Ag and β-cyclodextrin were studied. Fourier transformed infrared spectroscopy, thermogravimetric analyses and scanning electron microscope analysesof the prepared complexes were carried out. According to the results obtained, it was observed Fe_3O_4@HA@Ag especially forms inclusion complex with β-cyclodextrin at a mass ratio of 1:2. In the second part of this study, results related to the use of these inclusion complexes during electrospinning process in order to obtain antibacterial nanowebs, which could potentially be used in medical wounds, will be given.

Keywords: β-cyclodextrin, inclusion complex, Fe_3O_4@HA@Ag, scanning electron microscope

INTRODUCTION

Cyclodextrins (CDs) obtained as a result of enzymatic degradation of starch are a member of cyclic oligosaccharides. They have a number of hydroxyl groups [1]. Details on the position of hydroxyl groups and the cavities can be found elsewhere [2–3]. There are a significant number of CDs however the most common ones are α-, β-, and γ- CDs. Greek letters α-, β-, and γ- designate the number of glucopyranose units in their structure [4–7]. Due to their cone-shaped hydrophobic cavity, CDs are good candidates to be used as a host for molecule encapsulations to form inclusion complexes (ICs) [8–9]. Abdel-Halim et al. used β-CD as a host and loaded with octenidinedihydrochloride to form an IC which was then incorporated with a cotton fabric [10]. They investigated the antimicrobial property of IC-containing cotton fabric before and after each washes up to 20-wash. Inclusion complexes of CDs with different guest materials have been studied for a number of different applications [8, 11–13].

Silver and silver containing materials are widely studiedfor their antibacterial properties. Silver cyclohexane monocarboxylate (silver naphthenate), a product of naphthenic acid and silver salt reaction, was synthesized and its use as an antibacterial agent in textiles was investigated by Yildiz et al. [14]. A similar study was carried out on the synthesis of silver abietate to be used for antibacterial applications in textiles [15]. Silver and silver containing materials are also being used as the guest materials to form ICs with β-CD. Chen et al. used functionalized silver nanoparticles with β-CD to make possible to detect aromatic isomers by naked eye [16]. Antibacterial activity of silver nanoparticles hosted by β-CD was investigated by Andrade et al. together with structural and morphological characteristics of the inclusion complex [17].

Due to their electrical, magnetic and optical properties, magnetic nanomaterials have attracted the attention of researchers in recent years. These materials are good candidates for a number of applications. Role of Fe_3O_4 nanoparticles in biomedical applications was studied by Ghazanfari et al. [18] while magnetic nanocomposites consisting of Fe_3O_4, humic acid (HA) and silver (Ag) was synthezied by Amir et al. [19] for the purpose of azo dye removal from waste water of textile industry. In this study,

inclusion complexes containing Fe_3O_4@HA@Ag and β-cyclodextrin (guest:host) with mass ratios of 1:1 and 1:2 were prepared by using kneading and physical mixing techniques. Prepared complexes were then analyzed under FTIR, TGA and SEM. In the second part of this study, results related to the addition of these prepared inclusion complexes in nanofiber production with electrospinning technique.

EXPERIMENTAL WORK

Inclusion complexes of β-cyclodextrin with Fe_3O_4@HA@Ag were prepared according to the kneading technique at a mass ratio of 1:1 and 1:2. Mixtures of Fe_3O_4@HA@Ag:β-cyclodextrineat amass ratio of 1:1 and 1:2 by physical mixing technique were also prepared as reference. Mixing ratios and weights of the chemicals used in the inclusion complexes prepared are given in table 1.

Table 1

MIXING RATIOS AND WEIGHTS USED IN KNEADING AND PHYSICAL MIXING TECHNIQUES

Mass Ratio (gram)	Fe_3O_4@HA@Ag:β-CD (gram:gram)
1:1	0.113 : 0.113
1:2	0.113 : 0.226

The applications of kneading and physical mixing techniques are explained below.

• **Kneading technique**

In the kneading technique, firstly 1 mL of water was mixed with cyclodextrin. Fe_3O_4@HA@Ag was added on the cyclodextrin, and they were kneaded together on the mortar for 20 minutes. The amounts of chemical and cyclodextrin used varied according to the mixing ratio.

• **Physical mixing technique**

Cyclodextrin and chemicals to be used was stirred in a flask at room temperature for 5 minutes with the help of baguette at room temperature. The amounts of chemical and cyclodextrin used varied according to the mixing ratio.

Once these studies were completed, characterization tests were carried out to check if inclusion complexes were formed. For this aim FTIR, SEM and TGA analyzes were performed.

Fourier transformed infrared spectroscopy (FTIR) analyses: Samples were measured using a Thermo brand fourier alternating infrared spectrophotometerover the range 500–4000 cm^{-1}.

Scanning electron microscope (SEM) analyses: Quanta FEG 250 scanning electron microscope (FEI, Netherland) was employed for imaging of samples at a magnification of 1,000.

Thermogravimetric analyses (TGA): Samples were measured using a Perkin Elmer DSC 4000 thermogravimetric analyzer.

RESULTS AND DISCUSSION

FTIR results

The shape, shift change of the IR absorption peaks of the guest or the host (cyclodextrin) gives information on the formation of the inclusion complex [20]. FT-IR spectra of pure β-CD, pure Fe_3O_4@HA@Ag, physical mixtures and inclusion complexes prepared by kneading method both at 1:1 and 1:2 mass ratios are given in figure 1.

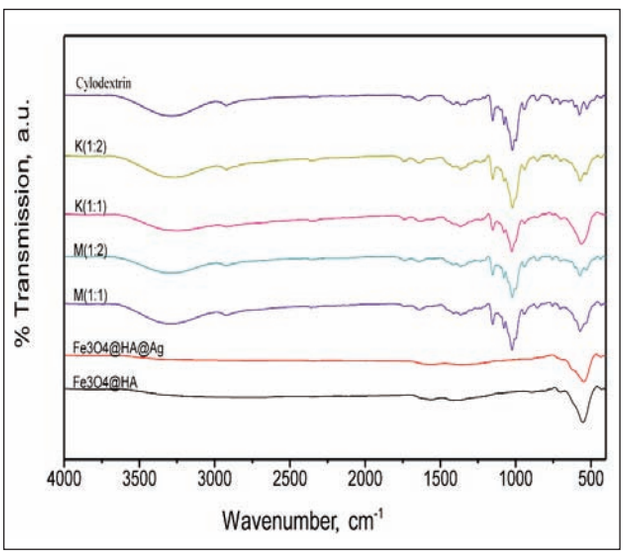

Fig. 1. FT-IR results of mixtures of Fe_3O_4@HA@Ag prepared with β-CD according to kneading and mixing techniques

As can be seen from figure 1, β-CD exhibited significant FT-IR peaks at wavelengths of 940 (skeletal vibrations involving α-1,4 bonds), 1090 and 1160 (v (CO), v (CC), v (COH) peaks), 1340 (H-CH) peaks), 1420 (δ (CH) peak from CH_2 and CH_3), 2930 (v CH peak) and 3300 v (-OH peak) cm^{-1} wavelengths [21]. When figure1 is examined, it is understood that the both 1:1 or 1:2 inclusion complexes of Fe_3O_4@HA@Ag and β-CD differs significantly from the FTIR curves of pure Fe_3O_4@HA@Ag and absorption bands of this inclusion complex is very similar with the pure β-CD. This indeed shows that the inclusion complex is formed and that significant shifts occur in its characteristic peaks due to the encapsulation of the Fe_3O_4@HA@Ag in β-CD cavity. These results actually indicate that there is some inclusion complex formation also in the physical mixing technique. When figure 1 is examined, it is noteworthy that complex preparation stoichiometry (1:1 and 1:2) has significant effect on the results obtained. It can be said that 1:2 complexes of β-CD with Fe_3O_4@HA@Ag gives better results.

TGA results

Thermograms of pure β-CD, pure Fe_3O_4@HA@Ag, theirphysical mixtures and inclusion complexes prepared by kneading method both at 1:1 and 1:2 mass ratios are given in figure 2.

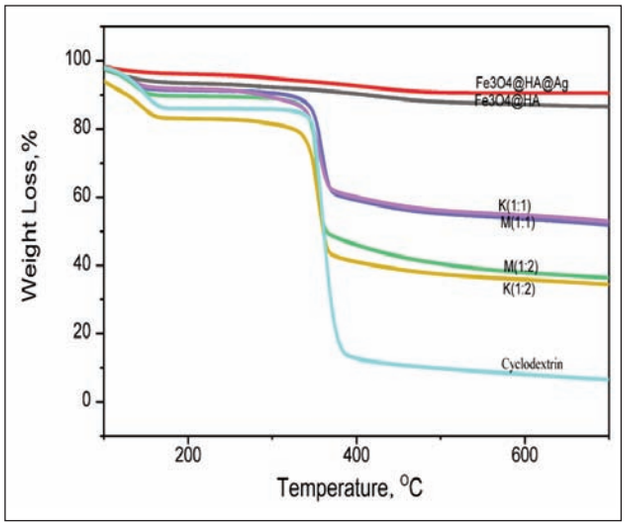

Fig. 2. TGA results of mixtures of Fe_3O_4@HA@Ag prepared with β-CD according to kneading and mixing techniques

When figure 3 is examined, it is understood that the both 1:1 or 1:2 inclusion complexes of Fe_3O_4@HA@Ag with β-CD differs significantly from the thermograms of Fe_3O_4@HA@Ag and absorption bands of these inclusion complexes are very similar with the pure β-CD. When the thermograms are examined, it can be seen that the thermal degradation result in pure β-CD causes a sharp mass loss at about 350°C. Normally, the thermal disruption of pure Fe_3O_4@HA@Ag does not result in a sharp mass loss, but a sharp mass loss at around 300°C occurs for their inclusion complexes with β-CD. This indeed shows that the inclusion complexes are formed and due to the encapsulation of Fe_3O_4@HA@Ag, significant shift in their heat distortion curves occurred.

SEM results

SEM analysis is ideal for measuring the surface roughness of the material and for visualizing surface texture [22]. For this reason, SEM photographs were taken for pure substances and prepared mixtures. SEM photos of pure β-CD, pure Fe_3O_4@HA@Ag, their physical mixtures and inclusion complexes prepared by kneading method both at 1:1 and 1:2 mass ratios are given in figure 3.

SEM photographs of Fe_3O_4@HA@Ag:β-CD complexes given in figure 3 show that both components are transformed into a collection of irregularly shaped

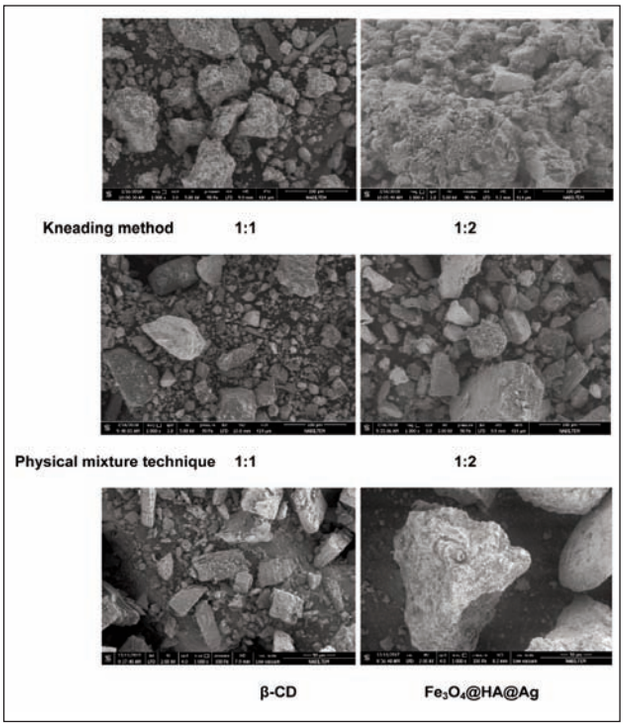

Fig. 3. SEM photos of mixtures of Fe_3O_4@HA@Ag prepared with β-CD according to kneading and mixing techniques (X1,000)

amorphous particles in which the original morphology disappeared [23].

CONCLUSION

In this study, the preparation of inclusion complexes according to kneading and physical mixing techniques at 1:1 and 1:2 (guest:host) mass ratios of Fe_3O_4@HA@Ag and β-cyclodextrin was studied. FTIR, TGA and SEM analyzes of the prepared complexes were carried out. According to the results obtained, it was found that Fe_3O_4@HA@Ag especially forms inclusion complex with β-cyclodextrin at a mass ratio of 1:2. As Electrospinning is one of the most widely used techniques in the 21st century, due to its adaptability and potential for applications in various domains, such as: wound healing, artificial skin, membranes for selective separation, target delivery system for active agents and molecules, scaffolds for tissue or bone engineering [24], in the second part of this study, results related to the use of these inclusion complexes during electrospinning process in order to obtain antibacterial nanofibers will be given.

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