

Magnetic nanoparticles embedded in pectin-based as an environmentally friendly recyclable nanocatalyst

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Abstract

Today, with the growth and development of human societies, increasing population and industrialization of countries, environmental pollution has increased and old methods of treatment are less responsive and the need to use new technologies to reduce pollution. One of these applications is the use of nanoparticles in the treatment of environmental pollutants. It is a nanoparticle that has dimensions between 1 and 100 nm. By reducing the particle size to less than 10 nm, the specific surface area and consequently their reactivity increases and this feature increases the refining capabilities of nanoparticles. The aim of this study was to describe some of the new properties and applications of catalyst nanoparticles with pectin substrate less than 10 nm in chemical reactions and to investigate the role of these nanoparticles in recent environmental developments, especially in the discussion of catalyst recycling in chemicals reaction. Designing a catalyst that combines the activity, selectivity, simple recovery, and follows the green chemistry instructions is of great importance. In the present study, Fe₃O₄@Pectin~CPTMS-Imidazole-Cu(II) was synthesized as an efficient and biopolymer-based magnetic catalyst for the oxidation of benzyl alcohols to aldehydes using tert-butyl hydroperoxide (TBHP) as an oxidant under solvent-free conditions. The catalyst was characterized using FT-IR, XRD, Fe-SEM, and TEM.

Keywords: Pectin, Nanocatalyst, Oxidation, Biopolymer

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Introduction

Exorbitant use of nonbiodegradable material and depletion of the planet's natural resources as well as environmental waste problems are convincing reasons to utilize greener sources like biopolymer-based material. [1, 2] Biopolymers (polynucleotides, polypeptides, and polysaccharides) are naturally-occurring polymers produced by living organisms. [3, 4] Due to their low cost, good stabilizing capability, and green nature, biopolymers have been widely used in biotechnology, agriculture, medicine, drug delivery, catalysis, textile, and industrial purposes [5-7]. Pectin is defined as linear polysaccharides consisting chiefly of D-galacturonic acid units

bagherzadeh@birjand.ac.ir, gbagherzade@gmail.com linked together with a (1-4)-glycosidic linkages called homogalacturonan (HG) [8]. The galacturonic acid residues may be methylated, acetylated, or amidated with different degrees [9]. As described anywhere, pectin has been used for many years in the food and beverages industry as a thickening and gelling agent as well as a colloidal stabilizer agent. The presence of free functional groups such as carboxyl and hydroxyl on the surface of pectin has enabled it to be used as a matrix for the delivery of various drugs, proteins, and cells [10]. In addition, the magnetization of bio-polymers is a very attractive way because it facilitates the separation of nanocatalyst from the reaction mixture and decreases the contamination of the final product caused by the presence of catalyst [11,12]. Thus, designing a catalyst that

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combines activity and selectivity at a lower cost and follows the green chemistry instructions is of great importance. In this paper, we would like to demonstrate a green, simple and inexpensive protocol for the oxidation of benzyl alcohols using TBHP as an oxidant and $\text{Fe}_3\text{O}_4\text{@Pectin}\sim\text{CPTMS}\text{-Imidazole}\text{-Cu(II)}$ as an efficient biopolymer-based magnetic nanocatalyst under solvent-free conditions (Scheme 1).

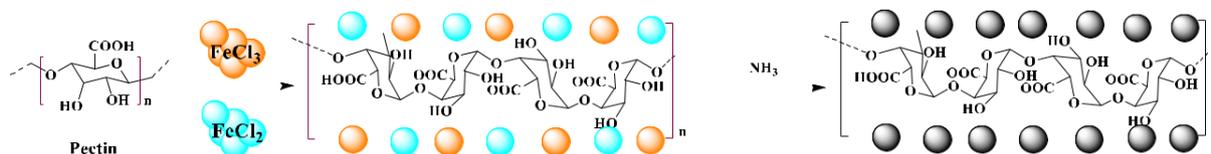
Experimental section and procedures:

All commercially available chemicals were purchased from Merck or Aldrich Company and used without further purifications. FT-IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer with using KBr pellet. Field emission scanning electron microscopy (FE-SEM) images were obtained on a HITACHI S-4160 microscope. Transmission electron microscopy (TEM) was performed on a Philips EM208 microscope operated at 100 kV. The X-ray diffraction (XRD) analysis of the powder samples

was performed on a Bruker AXS D8-advance X-ray diffractometer using $\text{CuK}\alpha$ radiation.

Preparation Magnetic Pectin ($\text{Fe}_3\text{O}_4\text{@Pectin}$)

First, pectin (1.0 g) was dissolved in 50 mL of distilled water and stirred for 2-3 h at room temperature to produce a white gelatine material. Then, a solution of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (3 g) and $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (1 g) dissolved in 120 mL distilled water was slowly added to the premixed solution under the ultrasonic irradiation. The obtained solution was then refluxed under the N_2 atmosphere at 90°C for 2 h. After that, 11 mL of 25% NH_3 was added slowly to the resulting mixture followed by stirring under the reflux at 90°C for 1 h. The obtained black precipitate was thoroughly washed with distilled water and ethanol to remove the unreacted materials and then dried at room temperature to produce the $\text{Fe}_3\text{O}_4\text{@Pectin}$ (Scheme 1).



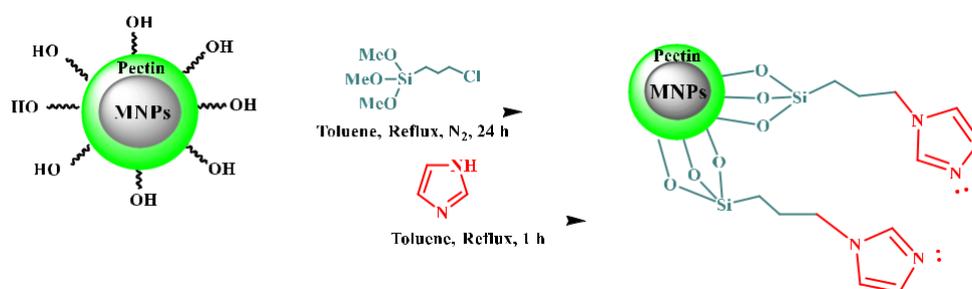
Scheme 1: synthesis of $\text{Fe}_3\text{O}_4\text{@Pectin}$

Preparation of CPTMS-Modified Magnetic Pectin ($\text{Fe}_3\text{O}_4\text{@Pectin}\sim\text{CPTMS}$)

Briefly, 1.0 g of $\text{Fe}_3\text{O}_4\text{@Pectin}$ nanoparticles were added to 10 mL dried toluene and dispersed by ultrasonic irradiation. Then, 2.5 mL of 3-chloropropyltrimethoxysilane (CPTMS) was added into the system and the mixture was stirred for 15 min followed by further stirring under the reflux for 24 h. After washing with toluene and water, the obtained magnetic nanoparticles were separated using an external magnet and dried at room temperature to prepare the ($\text{Fe}_3\text{O}_4\text{@Pectin}\sim\text{CPTMS}$) nanoparticles (Scheme 2).

Preparation of Imidazole-Functionalized Magnetic Pectin ($\text{Fe}_3\text{O}_4\text{@Pectin}\sim\text{CPTMS}\text{-Imidazole}$)

To prepare imidazole-functionalized magnetic pectin ($\text{Fe}_3\text{O}_4\text{@Pectin}\sim\text{CPTMS}\text{-Imidazole}$), the $\text{Fe}_3\text{O}_4\text{@Pectin}\sim\text{CPTMS}$ (1.9 g) nanoparticles were dispersed in dry toluene (20 mL) and sonicated for 15 min. To this solution, imidazole (0.24 g, 3.5 mmol) and sodium bicarbonate (0.672 g, 0.008 mol) were simultaneously added and the sonication was continued for 15 min. Subsequently, the mixture was refluxed for 24 h. After that, the product was separated by using an external magnet and thoroughly washed by dry diethyl ether (3×10 mL) to remove the unreacted substrates. Finally, the product ($\text{Fe}_3\text{O}_4\text{@Pectin}\sim\text{CPTMS}\text{-Imidazole}$) was then dried under vacuum at room temperature for 12 h.

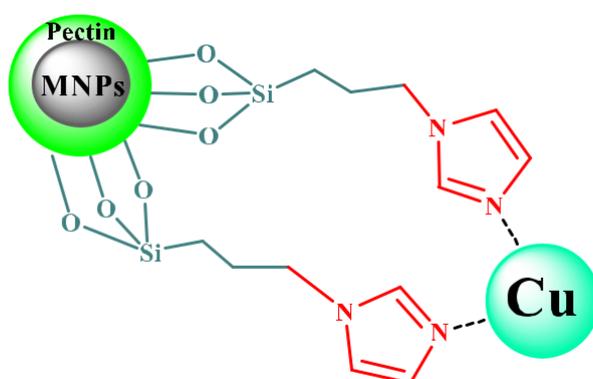


Scheme 2: synthesis of $\text{Fe}_3\text{O}_4\text{@Pectin}\sim\text{CPTMS}\text{-Imidazole}$

Cu(II) Immobilization on Fe₃O₄@Pectin~CPTMS-Imidazole

First, 1 g of Fe₃O₄@Pectin~CPTMS-Imidazole was dispersed in 10 mL dry toluene and sonicated for 30 min. To this solution, a mixture of Cu (OAc)₂ (0.9 g, 5 mmol) dispersed in 5 mL dry toluene was added slowly and the sonication was continued for 15 min followed by stirring under the reflux conditions for 24 h. After that, the product was separated by using an external magnet and washed

by dry diethyl ether (3×10 mL) to remove the unreacted substrates. The resulting catalyst was dried overnight under vacuum and the final obtained material was labelled as Fe₃O₄@Pectin~CPTMS-Imidazole-Cu (II). General description for the preparation of Fe₃O₄@Pectin~CPTMS-Imidazole-Cu (II) is shown in Scheme 3.



Scheme 3: synthesis of Fe₃O₄@Pectin~CPTMS-Imidazole-Cu

General Procedure for Benzyl Alcohol Oxidation using Fe₃O₄@Pectin~CPTMS-Imidazole-Cu (II) Nanocatalyst

A mixture of benzyl alcohol (1a-9a, 0.1 mL), *tert*-butyl hydroperoxide (TBHP, 0.2 mmol, 0.02 mL) and Fe₃O₄@Pectin~CPTMS-Imidazole-Cu (II) (1.5 mol%) was stirred at 40 °C for an appropriate time in solvent-free conditions to afford the corresponding aldehyde. After completion of the reaction, as monitored by TLC [eluent: n-hexane: ethyl acetate: 8:2], the reaction was cooled to room temperature and the catalyst was separated using an external magnet and the residue was concentrated to result in the corresponding aldehyde (1b-9b).

Result and discussion:

In this work, catalyst Fe₃O₄@Pectin~CPTMS-Imidazole-Cu (II) was prepared in several steps. At step one, the oxygen atom in the magnetite (Fe₃O₄) attacks the pectin as a nucleophile and a C-O bond was formed by the interaction between the Fe₃O₄ and the pectin. Then, silane, copper-metal complex added to the mixture of Fe₃O₄@Pect. Fe₃O₄, Fe₃O₄@Pect, Imidazole and Fe₃O₄@Pectin~CPTMS-Imidazole-Cu (II) was prepared (Scheme 1). Characterization of the Fe₃O₄@Pectin~CPTMS-Imidazole-Cu (II) structure was performed using various techniques such as FT-IR, FESEM, TEM, XRD, EDX and VSM. FT-IR spectra of (a) pectin, (b) Fe₃O₄@Pect, (c) Fe₃O₄@Pectin~CPTMS, (d) Fe₃O₄@Pectin~CPTMS-Imidazole and (e) Fe₃O₄@Pectin~CPTMS-Imidazole-Cu (II) are

shown in (Fig. 1). The FT-IR spectrum of pectin (Fig. 1a) shows the stretching vibrations of the O-H group at 3200-3450 cm⁻¹ and the stretching vibrations of the C=O, C-O group at around 1710 cm⁻¹ and 1120 cm⁻¹. As shown in the FT-IR spectrum of Fe₃O₄@Pect (Fig. 1b), the stretching vibrations Fe-O and O-H at 577 cm⁻¹ and 3420 cm⁻¹ confirmed the formation of Fe₃O₄ nanoparticles. Also, in the FT-IR spectrum of Fe₃O₄@Pectin~CPTMS (Fig. 1c), a new sharp peak at 1155 cm⁻¹ was assigned to the stretching vibration of Si-O. Immobilization of imidazole on the of Fe₃O₄@Pectin~CPTMS was confirmed by the peak appeared at 1641 cm⁻¹ (Fig. 1d), indicating that the imidazole is supported on the Fe₃O₄@Pectin~CPTMS. Furthermore, complexation of copper ions to imidazole causes the imine bond absorption 1641 cm⁻¹ to lower wavenumbers 1616 cm⁻¹ by about 25 cm⁻¹, indicating the participation of azomethine nitrogen in bonding with metal ion and confirming the coordination of ν(C=N) stretch to the metal via a nitrogen atom. The main absorption bands including (Fe-O), (Si-O), (C-N), (C=N) in the FT-IR spectrum of Fe₃O₄@Pectin~CPTMS-Imidazole-Cu (II) represent the successful functionalization of Fe₃O₄@Pect nanoparticles with imidazole and finally its complexation with Cu (II) (Fig. 1e).

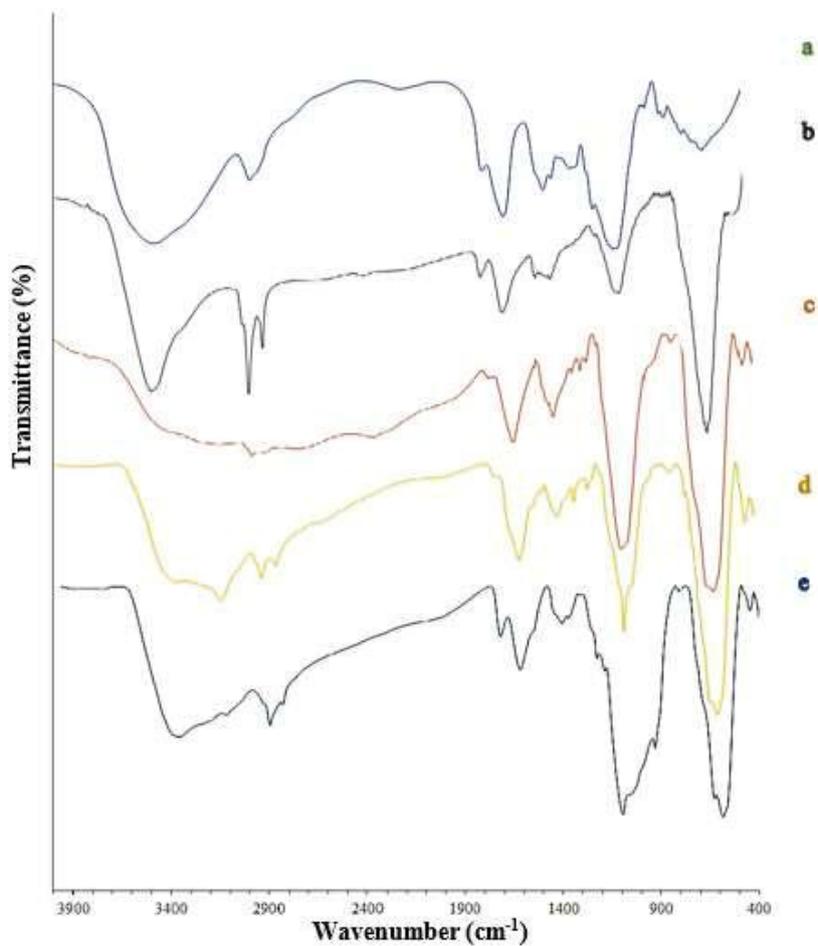


Figure 1: FT-IR spectrum of (a) Pectin, (b) Fe_3O_4 @Pectin, (c) Fe_3O_4 @Pectin~CPTMS, (d) Fe_3O_4 @Pectin~CPTMS-Imidazole (e) Fe_3O_4 @Pectin~CPTMS-Imidazole-Cu (II)

Particle size and the morphology of Fe_3O_4 @Pectin~CPTMS-Imidazole-Cu (II) were discovered using Fe-SEM and transmission electron microscopy (TEM) analysis. Fe-SEM and TEM micrographs indicated that Fe_3O_4 @Pectin~CPTMS-Imidazole-Cu (II) nanocomposites were made up of almost

aggregated spheroidal-shaped particles. Also, most of the nanoparticles were in the range of 15-25 nm diameters (Fig. 2).

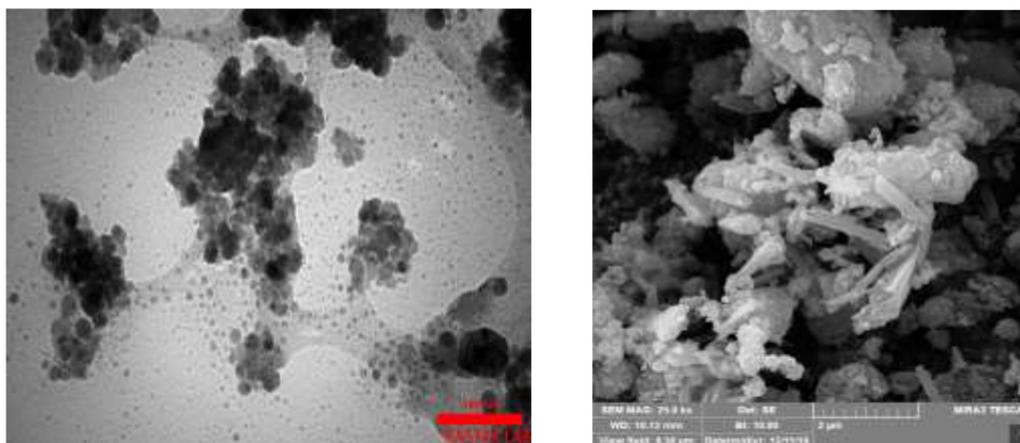


Figure 3: FE-SEM (right) and TEM (left) image of the Fe_3O_4 @Pectin~CPTMS-Imidazole-Cu (II)

The X-ray diffraction pattern of $\text{Fe}_3\text{O}_4@\text{Pectin}\sim\text{CPTMS}\text{-Imidazole-Cu (II)}$ is shown in (Fig. 4). Figure 4a shows the magnitude of the magnetic nanoparticles using the markers (220), (311), (400), (422), (511) and (440) that the magnetic nanoparticles are Fe_3O_4 and have an

inverted spinel structure. [13] Weak and strong peaks at $2\theta = 20\text{-}25^\circ$ crystallographic phases in XRD pattern are related to Pectin of catalyst $\text{Fe}_3\text{O}_4@\text{Pectin}\sim\text{CPTMS}\text{-Imidazole-Cu (II)}$.

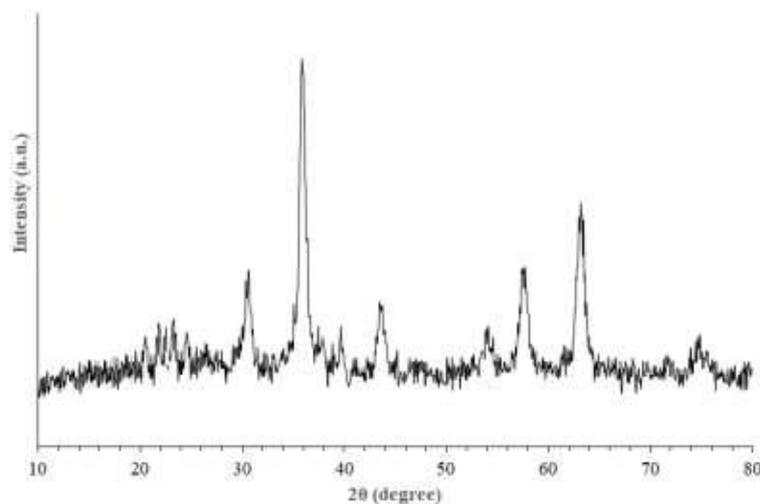


Figure 4: XRD pattern of $\text{Fe}_3\text{O}_4@\text{Pectin}\text{-CPTMS}\text{-Imidazole-Cu (II)}$

Oxidation of benzyl alcohols

The catalytic activity of $\text{Fe}_3\text{O}_4@\text{Pectin}\sim\text{CPTMS}\text{-Imidazole-Cu (II)}$ was initially evaluated in a standard reaction using benzyl alcohol (1 mmol) and the effect of changes in various parameters. After the study of organic and aqueous solvents, the best result is 95% yield in solvent-free conditions. Catalyst loading, TBHP, temperature, and time reaction conditions give 2 mol%, 2 mmol,

40 °C, and 60 minutes for this reaction, respectively. With these optimal reaction conditions in hand, we studied the amplitude of the substrate. The results shown in Table 1 confirm the efficacy of this method for different benzyl alcohols (entry1-5) by electron donation and electron extraction groups.

Table 1: Oxidation of various alcohols using TBHP and $\text{Fe}_3\text{O}_4@\text{Pectin}\sim\text{CPTMS}\text{-Imidazole-Cu (II)}$ magnetic nanocatalyst.

Entry	Substrate	Product	Time (min)	Yield ^a (%)
1			60	95
2			60	92
3			45	90
4			45	92
5			60	88

^a Isolated yield.

Conclusion

As a result, a new approach to the preparation of new magnetic pectin has been reported, which is an easy, general, cost-effective, and environmentally friendly method used as a green catalyst for the oxidation of alcohols. Finally, the magnetic catalyst was easily recovered from the reaction mixture and reused five times in a row without loss of usable reaction.

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