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Magnetized Dextrin: Eco-Friendly Effective Nanocatalyst for the Synthesis of dihydropyrano[2,3-c]pyrazole Derivatives †

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Abstract: Dextrin is a water soluble polysaccharide obtained by hydrolysis of starch and glycogen. This low molecular weight biopolymer with valuable properties such as biodegradability, natural origins, good availability and high reactivity can be an appropriate substance to fabricate the environmentally friendly catalysts. The magnetized dextrin was prepared via facile co- precipitation procedure of iron salts in the presences of dextrin under alkaline condition. Then, it was characterized by different conventional analyses. Eventually, the catalytic application of obtained nanocomposite was evaluated for the synthesis dihydropyrano[2,3-c]pyrazole derivatives through multicomponent reaction of hydrazinehydrate, ethyl acetoacetate, aromatic aldehydes and malononitrile. Biocompatible nanocatalyst, simple procedure, short reaction times, and catalyst reusability after four consecutive runs with negligible decrease in catalytic efficiency are some merits of presented method.

Keywords: Dextrin; eco-friendly catalyst; multicomponent reaction; pyranopyrazole

1. Introduction

One of the important achievements of the principles of green chemistry is the design and fabrication of biocompatible catalysts [1]. Dextrin is a low molecular weight polysaccharide with chemical formula $(C_6H_{10}O_5)_n$ which is obtained from the hydrolysis of starch or glycogen Dextrin is composed of D-glucose units linked by α-(1 → 4) or α-(1 → 6) glycosides bonds (Figure 1) [2]. As a natural polymer, dextrin has outstanding properties for instance have great number of hydroxyl groups, water solubility, biodegradability, good stability, low cost and non-toxicity. Therefore, it has been used in environmental chemistry, biochemistry, pharmaceutical chemistry and more recently in catalysts [3].

The presence of a large number of reactive functional groups in its chemical structure provided chemical modification to fabricate the diverse compounds and composites of this material with catalytic potential application. In this work, a composite consisting of dextrin and Fe_3O_4 MNPs prepared via simple procedure. This composite has the advantages of dextrin, especially the presence of large number of hydroxyl groups that can form a hydrogen bond with the starting reactants and accelerate the reaction, also has the advantages of Fe_3O_4 MNPs such as high surface area, Lewis acid sites and the possibility of recovery and reusability. Multicomponent reactions (MCRs) are one of the most important approach to construct the organic compounds which offer outstanding benefits such as high atomic efficiency, time and energy saving, and environmentally friendly [3,4]. Dihydropyrano [2,3-c]pyrazole is a heterocyclic compound with potential application in medicinal and pharmaceutical chemistry and significant role as building blocks in the preparation of valuable drugs such as antimicrobial, antiviral, analgesic, anti-inflammatory, anticancer and anti-proliferative

[5]. In continues to our research on MCRs and nanomaterials[6–8], in present work, magnetized dextrin was used as a hybrid nanocatalyst in the synthesis of dihydropyrano[2,3-c]pyrazoles derivatives, via one-pot condensation of ethyl acetoacetate, hydrazinehydrate, malononitrile and aromatic aldehydes (scheme 1).

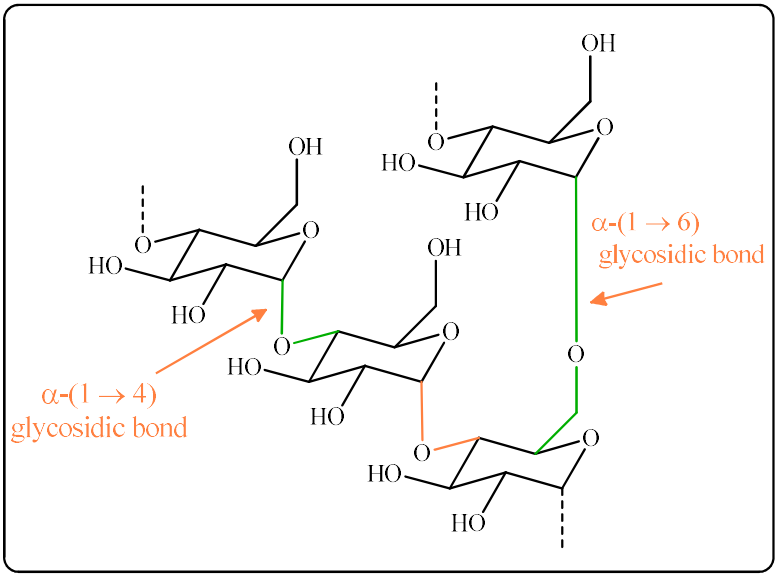
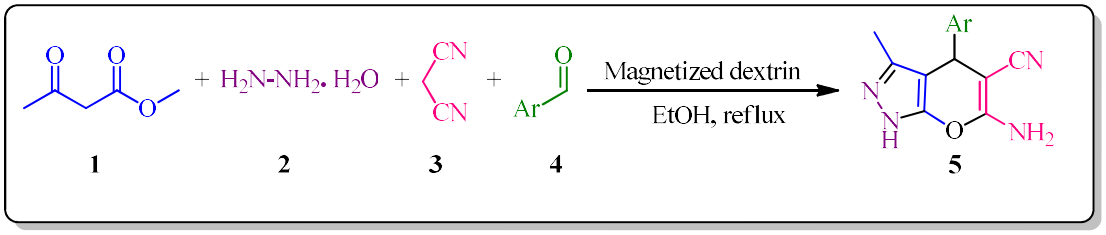


Figure 1. Chemical structure of dextrin.



Scheme 1. The synthesis of dihydropyrano[2,3-c]pyrazoles derivatives.

2. Experimental

2.1. General

All chemicals were purchased from Merck and Aldrich companies. The melting points of the prepared derivatives were measured by an electrothermal 9100 apparatus. Elemental analysis of the nanocatalyst was carried out by energy-dispersive X-ray (EDX) analysis recorded on Numerix JEOL-JDX. X-ray diffraction (XRD) pattern of the nanocatalyst was recorded on an X-ray diffractometer (Bruker D8 Advance) and the morphology of prepared nanocatalyst was studied by SEM usingVEGA2 TESCAN instrument.

2.2. Preparation of Magnetized Dextrin Nanocomposite

First, 2 mmol $FeCl_3.6H_2O$ and 1 mmol $FeCl_2.4H_2O$ were dissolved in 100 mL of distilled water, then the aqueous solution of 0.35 g dextrin in 25 mL distilled was added to the solution. The temperature of resulting mixture was raised to 90 °C and stirred under nitrogen atmosphere for one hour. Later, NH_4OH (25%) was added dropwise over 15 min to the stirring above suspension The reaction continued for about one hour. Finally, the black crude precipitate was collected by magnet,

washed several times with distilled water and ethanol to remove non-reactive materials, and then dried at room temperature for 6 hours to obtain magnetized dextrin nanocomposite.

2.2. General Procedure for the Synthesis of dihydropyrano[2,3-c]pyrazole Derivatives

The mixture of hydrazinehydrate (2 mmol), ethyl acetoacetate (2 mmol), malononitrile (1 mmol) and aromatic aldehydes (1 mmol) were mixed together in the presence of 0.015 g of magnetized dextrin in ethanol and refluxed for appropriate time. The reaction progress was monitored by thin layer chromatography (TLC). Finally, after completion of the reaction, the catalyst was separated from the reaction mixture through an external magnet and high pure product was obtained by recrystallization of the crude precipitate in ethanol.

3. Results and Discussion

3.1. Characterization Magnetized Dextrin

Elemental analysis was employed to investigate the chemical composition of the magnetized dextrin. As can be seen in the Figure 2, the presence of C, O and Fe elements in the prepared nanocatalyst was confirmed by this analysis.

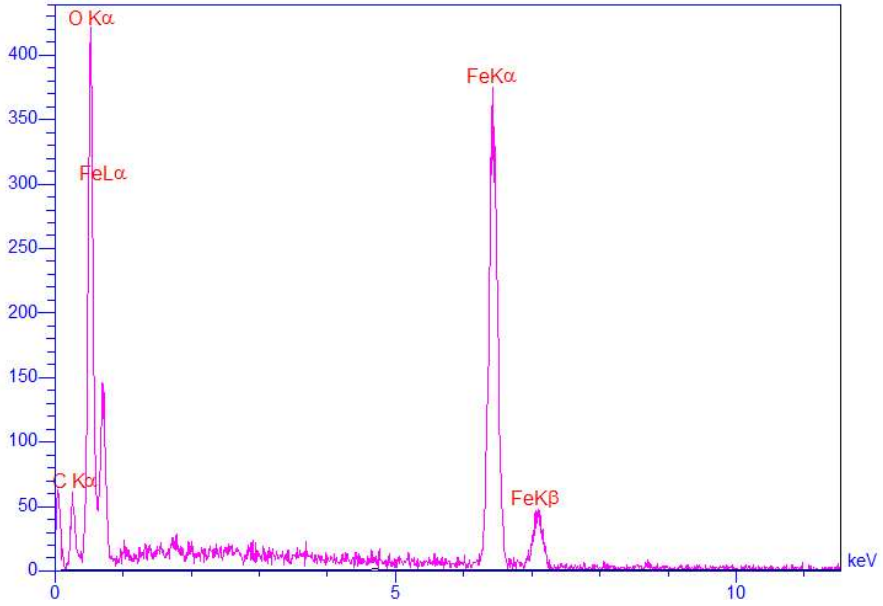


Figure 2. (**a**) EDX analysis of magnetized dextrin nanocatalyst.

FT-IR spectra of magnetized dextrin (b) in comparison with dextrin (a) are observed in Figure 3. In the spectrum of dextrin, a broad absorption band at 3438 cm^{-1} is related to the stretching vibration of O–H bond which is abundant in dextrin structure, adsorption band at 2923 cm^{-1} is related to the stretching vibration of C–H bond, and the adsorption band at 1153 cm^{-1} is attributed to the asymmetric vibration of the glycosidic C–O–C bond. Comparison of FT-IR spectra of magnetized dextrin and dextrin showed that, in the magnetic dextrin spectrum, in addition to observing the main adsorptions of dextrin, two new absorptions at 632 and 579 cm^{-1} appeared which is ascribed to the stretching vibrations of Fe–O bond of Fe_3O_4 MNPs [3].

The SEM image was used to show the morphology and particle size of the prepared nanocatalysts. As is shown in Figure 4, there are aggregation of spherical like particles which ascribed to Fe_3O_4 MNPs, dispersed on the surface of dextrin. The average particle size of a magnetized dextrin is about 85 nm.

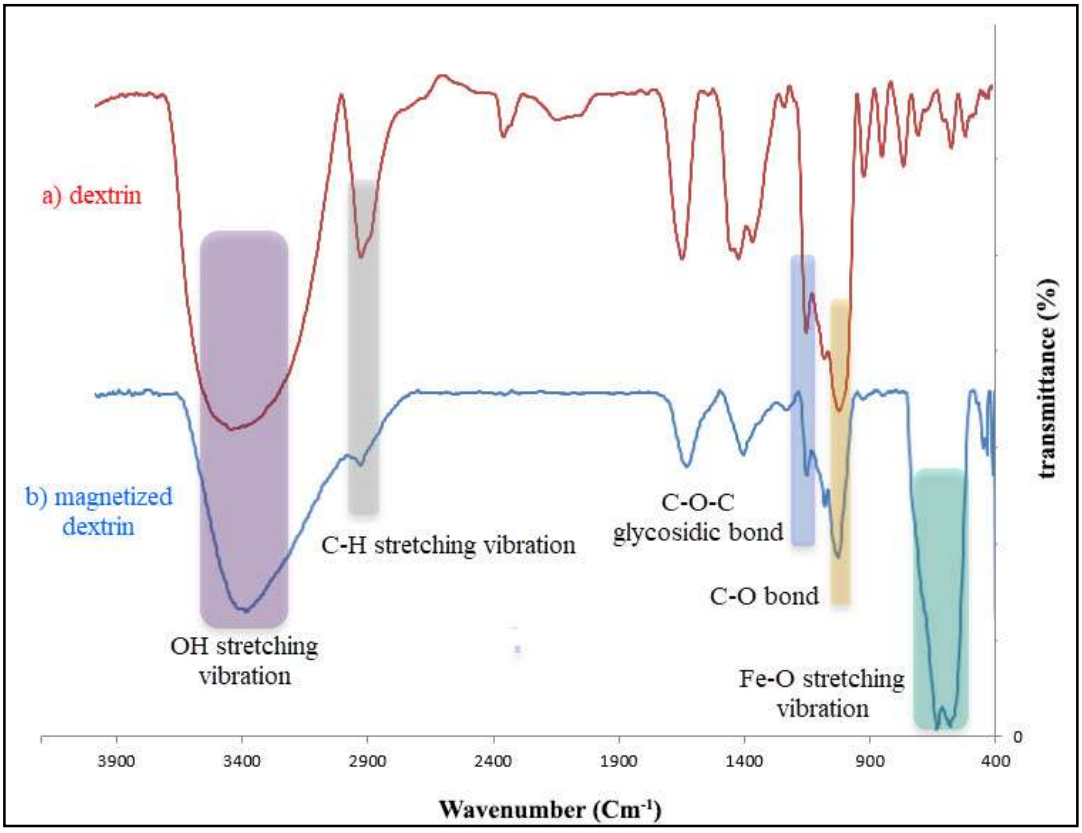


Figure 3. FT-IR spectra of dextrin and the magnetized dextrin nanocatalyst.

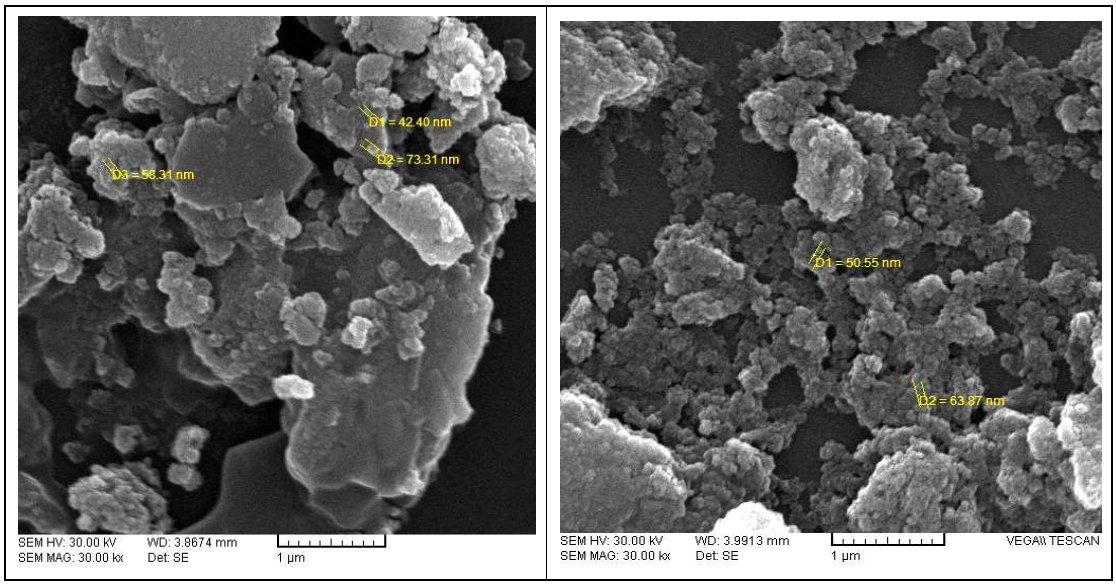


Figure 4. SEM images of the magnetic dextrin nanocatalyst.

XRD analysis was used to study the crystalline structure of prepared nanocatalyst. As reported in the literature, XRD pattern of dextrin has two broad peaks signifying its amorphous nature [9]. The XRD patterns of magnetized dextrin and standard Fe_3O_4 MNPs were compared in Figure 5. The synthesized nanocomposite exhibited several peaks at 2θ = 17.5°, 30.1°, 35.5°, 37.9°, 57.4° and 69.7° that are in accordance with the standard pattern of Fe_3O_4 MNPs with card no. JCPDS, 00-001-111.

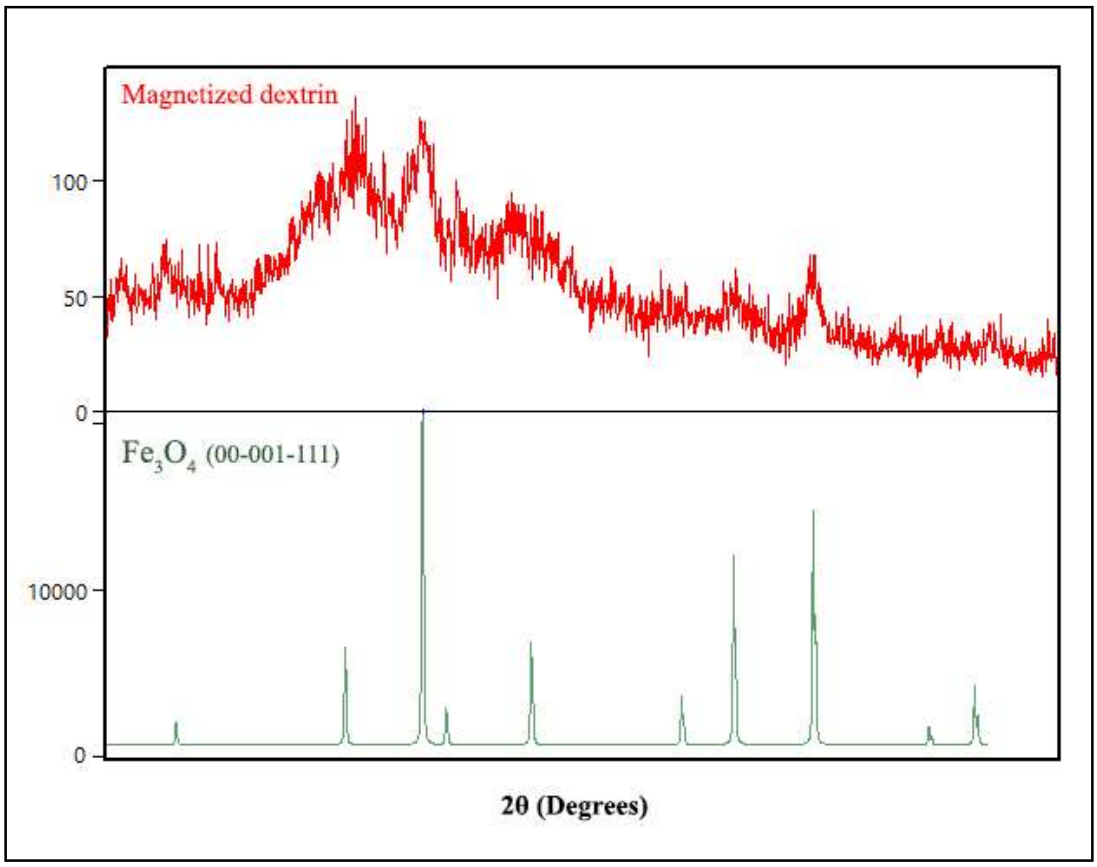


Figure 5. the XRD pattern of the magnetized dextrin nanocatalyst and standard Fe_3O_4.

3.2. Catalytic Application of the Magnetized Dextrin in the Synthesis of dihydropyrano[2,3-c]pyrazole Derivatives

The synthesis of dihydropyrano[2,3-c]pyrazole derivatives using some aromatic aldehydes in optimum condition was studied and in order to evaluate generality, and limitation of this protocol. As is observed in Table 1, all examined aromatic aldehydes with electron withdrawing and electron donating substitution produced the satisfying corresponding products.

Table 1. The synthesis of dihydropyrano[2,3-c]pyrazole using the magnetized dextrin nanocatalyst.

Entry	R	Product	Yield [a] (%)	Mp (°C)
1	4-Cl	**4a**	92	232–235 [5]
2	3-NO_2	4b	90	236–239 [5]
3	4-OMe	4c	85	212–214 [5]
4	3-OMe	4d	89	245 [10]
5	4-Me	4e	84	193–195 [10]

[a] Isolated yield.

4. Conclusions

Magnetized dextrin nanocomposite was synthesized using as a green, retrievable and cost-effective catalyst for synthesis of biologically active of dihydropyrano[2,3-c]pyrazole derivatives. This procedure has advantages such as high efficiency products, mild reaction conditions and easy separation of the product from the reaction mixture.

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