



Synthesis of Fe₃O₄/Eggshell Nanocomposite and Application for Preparation of Tetrahydrobenzo[b]Pyran Derivatives

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ABSTRACT

This work is reported on the synthesis of Fe₃O₄/eggshell nanocomposites in the absence of any stabilizer or surfactant. Fe₃O₄ magnetic nanoparticles were established on the egg shell nanocomposite. The nanocomposites have shown high catalytic activities in the synthesis of Tetrahydrobenzo[b]pyran. These derivatives were synthesized via an one-pot three-component condensation of aromatic aldehydes with malononitrile and dimedone with excellent yields in the presence of Fe₃O₄/eggshell nanocomposites as a highly efficient heterogeneous catalyst. The obtained catalyst was characterized by Fourier transform infrared spectroscopy (FT-IR), Field emission scanning electron microscopy (FE-SEM), X-ray diffraction analysis (XRD) and Vibrating sample magnetometer (VSM). The developed technique of nano-composite synthesis is energy efficient since the reactions carried out in single step. The present catalyst is possible to be used for the production of biodiesel.

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INTRODUCTION

Single step multicomponent reactions (MCRs) by advantage of their convergence, usefulness, facile extinction and generally high yield of products have attracted significant attention from the point of view of ideal synthesis [1]. The first MCR was initiated by Strecker in 1850 for the synthesis of amino acids [2]. However, in past decades there were great developments in MCRs and significant efforts were made to find and form new MCRs [3]. Tetrahydrobenzo[b]pyran derivatives are a significant category of heterocyclic compounds with effective biological and pharmacological properties. These compounds have been widely used as anticoagulant, antitumor, spasmolytic, antibacterial, diuretic, potassium channel activator and insulin-sensitizing activity [4-9]. Several methods for the synthesis of tetrahydrobenzo[b]pyran derivatives have been reported for instance 4H-benzo[b]pyrans were synthesized from α -cyanocinnamionitrile derivatives in a single step reaction which is catalyzed by acid or base [10-12]. Several methods stated for the synthesis of these compounds in the presence of catalysts such as sodium bromide [13], hexadecyldimethylbenzylammonium bromide [14], tetramethylammonium hydroxide [15], diammonium hydrogen phosphate [16], fluoride ions

[17], magnesium oxide [18], sodium selenite [19], iodine [20], H₆P₂W₁₂O₆₂·H₂O [21], tetrabutylammonium bromide [22], cerium(III) chloride [23]. However, each of the above-mentioned methods has a drawback such as: long reaction time, severe reaction conditions, use of toxic reagents and low reaction yield. Thus, the development of fast, suitable, and environmentally friendly methods for the synthesis of tetrahydrobenzo[b]pyrans remains an essential strategy to overcome stated problems. The strategy of the use of waste materials has an amazing upsurge of good intention in the application of bio-waste materials such as eggshell waste. Low-cost eggshell waste has been widely used as a possible bone substitute, catalyst, support, and efficient bio-templates due to their high catalytic activity, ease of handling, reusability and benign character [24-39]. The eggshell is an inexpensive and easily available biomaterial; it has a porous structure that is related to its natural content. According to the literature, chemical compounds found in egg shell are calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) [40]. It is individually attractive for synthesizing metal nanoparticles due to strong metal-protein bonding can be readily employed [24-39]. Nowadays, waste shell of egg support has been employed as a catalyst for biodiesel synthesis, lactose isomerization and preparation of dimethyl carbonate [41-

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44]. Magnetic nanoparticles have been used in various fields for example drug delivery, magnetic resonance imaging contrast enhancement, data storage, targeted drug, magnetic bio separation because of their excellent properties of super paramagnetism, low toxicity, high magnetic susceptibility, biocompatibility, and high saturation magnetization [45-52]. In this work, an attempt was made to investigate catalytic activity of Fe_3O_4 /eggshell nanocomposite from waste chicken eggshell on synthesis of tetrahydrobenzo[*b*]pyrans. More importantly, the synthesized Fe_3O_4 /eggshell nanocomposite possessed good magnetic property, which is easily separated from the reaction mixture using a magnet. Utilization of such property would be useful and reused for 5 cycles without loss of its catalytic activity, indicative of a potential application in industry.

MATERIAL AND METHODS

All materials were purchased from Merck (Germany) and Aldrich chemical (USA). The chemicals were used without further purification; eggs from hens were purchased from a local supermarket. FT-IR spectra were recorded on a Nicolet 370 FT-IR spectrometer (Thermo Nicolet, USA) using pressed KBr pellets. The natural zeolite used in this study was originated from local market. X-ray diffraction (XRD) measurements were carried out using a Philips powder diffractometer type PW 1373 goniometer ($\text{Cu K}\alpha = 1.5406 \text{ \AA}$). The scanning rate was $2^\circ/\text{min}$ in the 2θ range from 10 to 80° . Scanning electron microscopy (SEM) was performed on a Cam scan MV2300. EDS (S3700N) was utilized for chemical analysis of prepared nanostructures. VSM (Vibrating sample magnetometer) measurements were performed by using a SQUID magnetometer at 298 K (Quantum Design MPMS XL). NMR spectra were recorded using a Bruker Avance DRX 400 MHz instrument. The spectra were measured in DMSO- d_6 relative to tetramethylsilane (0.00 ppm).

Preparation of Fe_3O_4 magnetite doped eggshell membrane

The crushed fresh eggshell was incubated in diluted 1% acetic acid at 22°C for 1 h. Afterward the eggshell membrane (EM) was easily separated and cut into small pieces (1 cm^2). It was cleaned with copious amount of twice distilled water. Then, the preparation of Fe_3O_4 magnetic doped eggshell membrane was placed on dissolving $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (11.68 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4.30 g) in 200 mL deionized water. This solution was stirred with magnetic stirrer (2000 rpm) at 50°C for 1 h. Nitrogen gas was continuously bubbled through this solution for the removal of dissolved oxygen. Then, the EM was immersed in solution following that, 10 mL of 25% NH_3 was rapidly added to the solution. After that, the color of bulk solution turned immediately from

orange to black. The magnetite eggshell membrane (MESM) were collected by a magnet after washing several times with deionized water and ethanol solution. Finally, the products were dried in oven at 50°C for 12 h.

General procedure for synthesis of tetrahydrobenzo[*b*]pyran derivatives

A mixture of an aromatic aldehyde (1.1 mmol), malononitrile (1.0 mmol), dimedone (1.0 mmol), and catalyst (50 mg), was dissolved in H_2O -EtOH (1:1) and was stirred at 60°C . The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature (RT), and diluted with water. The catalyst was easily separated from the reaction mixture with an external magnet. The crude products were recrystallized from ethanol and pure products were obtained.

RESULTS AND DISCUSSION

The structure and morphology of Fe_3O_4 /eggshell magnetic nanocatalyst were analyzed by XRD and SEM. Figure 1 shows a characteristic XRD pattern of the Fe_3O_4 /eggshell, the main peak was observed at $2\theta = 29.5$ and other peaks were observed at $2\theta = 36.2, 40.1, 44.2, 48.7, 57.7$ and 62.1 . Corresponds to the (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 4 0) and (5 1 1) are readily recognized from the XRD pattern; which could be indexed to a face-centered cubic of CaCO_3 (JCPDS, no. 5-0586). Further, diffraction peaks at $2\theta = 36.1^\circ, 43.7^\circ, 54.6^\circ, 58.1^\circ$ and 61.4° appear in the XRD pattern of the Fe_3O_4 /eggshell, which can be assigned to the diffraction of (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes of the cubic Fe_3O_4 . These peaks were compared to the Joint Committee on Powder Diffraction Standards (JCPDS no. 19-629) file.

The average crystallite/grain size is estimated using Debye-Scherrer formula [$D = k\lambda/\beta \cos(\theta)$] where D is average crystal size, k is the Scherrer coefficient (0.9), λ is the X-ray wavelength ($\lambda = 1.54 \text{ \AA}$), β is the full width half maximum intensity (FWHM) and θ is the diffraction angle [28]. From the Scherrer equation the average crystalline/grain size of Fe_3O_4 -nano particle (NP) is 24 nm.

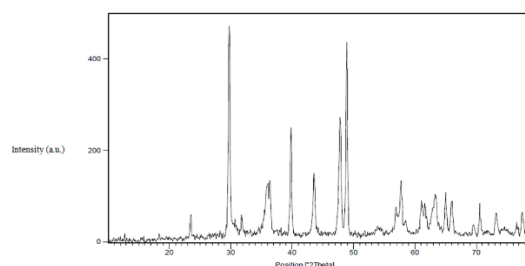


Figure 1. XRD pattern of the Fe_3O_4 /eggshell Catalyst.

The magnetic properties of Fe₃O₄/eggshell were characterized by a vibrating sample magnetometer (VSM). The saturation magnetization of Fe₃O₄ NPs at room temperature, with the field sweeping from -10000 to +10000 Oe. As shown in Figure 2, the value of magnetic saturation for the Fe₃O₄/eggshell is 65.5 emu g⁻¹, the catalyst can be efficiently separated from the solution with an external magnetic force.

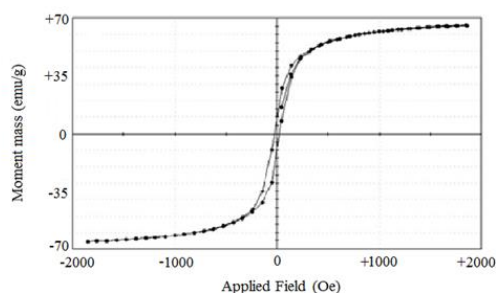


Figure 2. VSM Curve for Fe₃O₄/eggshell at room temperature.

FT-IR analysis of Fe₃O₄/eggshell was performed and is shown in Figure 3. A thorough study on FT-IR spectra has been reported by Engin et al. [53], where in the catalyst the major absorption bands occurred at 1415, 879, and 700 cm⁻¹, which are attributed to asymmetric stretch, out of plane bend and in plane bend vibration modes, for CO₃²⁻ molecules. The absorption bands situated at 3000–2500 cm⁻¹ marked with asterisks in spectrum were also attributed to organic matter [53]. The peaks centered around 3400 cm⁻¹ and 1620 cm⁻¹ are, respectively, assigned to the O-H stretching and deforming vibrations of Fe₃O₄ and the peak at 578 cm⁻¹ are corresponding to the Fe-O vibration.

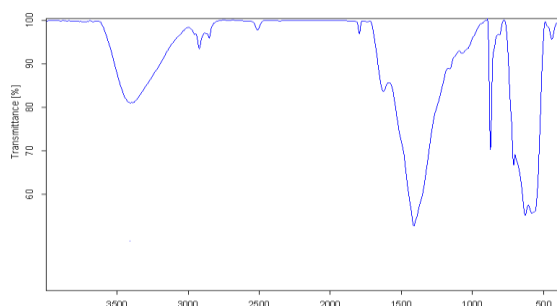


Figure 3. FT-IR Spectra of Fe₃O₄/eggshell.

The morphology of the sample was investigated with scanning electron microscopy (SEM). Figure 4 shows spherical structure Fe₃O₄/eggshell catalyst.

Optimization for the catalyst synthesis

In order to optimize the reaction conditions, the reaction of benzaldehyde (1 mmol), malonitrile (1 mmol), and dimedone (1 mmol) were carefully investigated. Tables 1 and 2 summarized the different ratio of solvent (H₂O,

EtOH) and the various amount of catalyst were experimented. The best results were obtained at 70 °C in the presence of 60 mg catalyst in H₂O-EtOH (1:1).

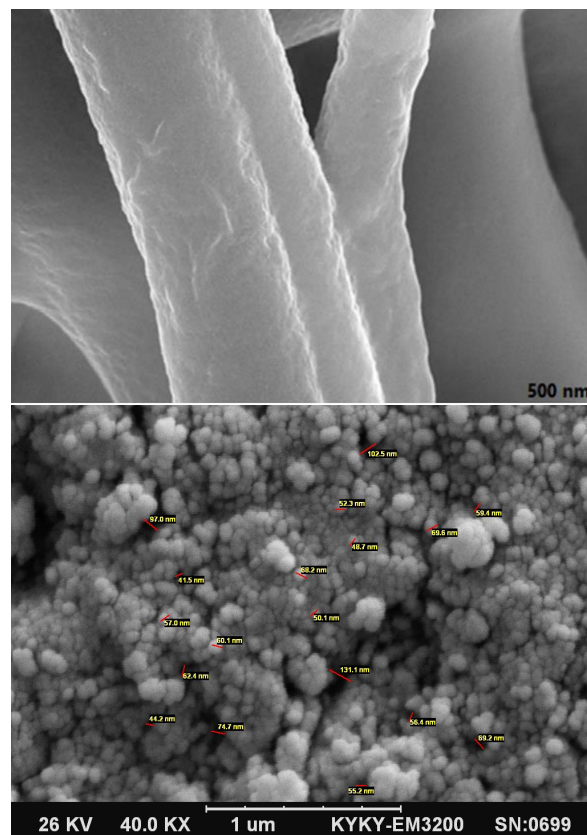


Figure 4. TEM & SEM Images of Fe₃O₄/eggshell.

TABLE 1. Effect of amount of catalyst on synthesis

Entry	Solvent	Time(min)	Yield(%) ^b
1	H ₂ O	120	45
2	EtOH	80	65
3	EtOH/H ₂ O (1/2)	60	70
4	EtOH/H ₂ O (2/1)	50	80
5	EtOH/H ₂ O (1/1)	40	98

^aReaction conditions: 2,4 di-chlorobenzaldehyde (1 mmol), malonitrile (1 mmol), dimedone (1 mmol), and catalyst at 70 °C.

^bYields refer to isolated pure product.

TABLE 2. Effect of amount of catalyst on synthesis of tetrahydrobenzo[b]pyran derivatives at 70 °C.^a

Entry	Catalyst (mg)	Yield (%) ^b
1	20	50
2	40	75
3	60	98
4	80	98

^aReaction conditions: 2,4 di-chlorobenzaldehyde (1 mmol), malonitrile (1 mmol), dimedone (1 mmol), and catalyst at 70 °C.

^bYields refer to isolated pure product.

The scope and efficiency of the reaction under optimum conditions were explored for the synthesis of a wide variety of substituted tetrahydrobenzo[*b*]pyran derivatives from aryl aldehydes, malononitrile, and dimedone (Figure 5). The results are summarized in Table 3. Substituents on the aromatic ring show electronic effects in terms of yields under these reaction conditions. The reactions proceeded smoothly and produce good yields. The aromatic aldehyde bearing electron-donating group such as OMe, reacted much slower with malononitrile and dimedone than other aromatic aldehydes substituted with electron withdrawing groups such as NO₂⁻ and Cl⁻.

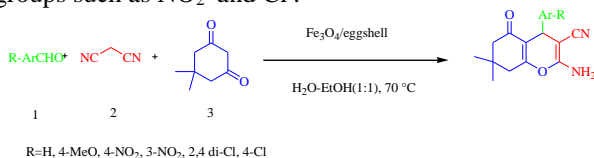


Figure 5. Single step synthesis of 4*H*-drobenzo[*b*]pyran derivatives catalyzed by Fe₃O₄/eggshell.

TABLE 3. Synthesis of tetrahydrobenzo[*b*]pyran derivatives via condensation of aryl aldehydes (1), malononitrile (2), and dimedone (3) in the presence of catalyst in H₂O-EtOH (1:1) at 70 °C.

Entry	Ar	Time (min)	Yield (%)
1	C ₆ H ₅	50	80
2	4-MeOC ₆ H ₄	70	75
3	3-NO ₂ C ₆ H ₄	30	92
4	4-NO ₂ C ₆ H ₄	25	98
5	2,4-ClC ₆ H ₃	30	92
6	4-ClC ₆ H ₄	40	90

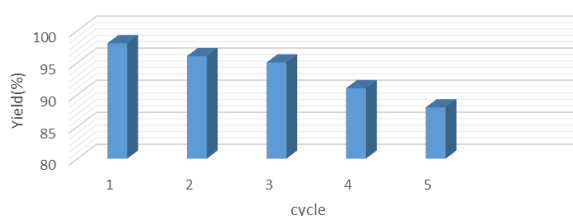


Figure 6. Reusability of catalyst. Reaction conditions: 2,4 di-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), dimedone and Fe₃O₄/eggshell (50 mg) at 70°C.

After the reaction was completed, the catalyst was recovered using an external magnet, and in order to be reused. The reused catalyst was washed with ethanol for several times and then dried. The catalyst showed no significant losses in catalytic activities for five cycles use (Figure 6).

CONCLUSION

In this work, we have developed a simple and efficient method for the synthesis of tetrahydrobenzo[*b*]pyran derivatives with different aldehydes using magnetic recoverable Fe₃O₄/eggshell at mild conditions. The catalyst is completely recoverable due to the superparamagnetic behavior of Fe₃O₄ and the efficiency of the catalyst remains unaltered even after 5 cycles used. The facile synthesis, excellent properties, alterable supports and low costs allow these nanocomposites to be used for the synthesis of tetrahydrobenzo[*b*]pyran derivatives.

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Persian Abstract

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چکیده

در این کار بر روی سنتز نانوذرات پوسته تخم مرغ / Fe_3O_4 به صورت نانو کامپوزیت در غیاب هر گونه تثبیت کننده و یا سورفاکتانت گزارش شده است. نانوذرات مغناطیسی Fe_3O_4 روی اسیدیتته نانو کامپوزیت پوسته تخم مرغ ایجاد شده است. این نانو کامپوزیت‌ها، فعالیت کاتالیزوری بالا در سنتز Tetrahydrobenzo [B] pyran نشان داده شده است. این مشتقات با استفاده از یک ترانس مولکولی سه جزء آلدهید آروماتیک با مالونونیتریل و دی میدون در تولید نانو کامپوزیت های پوسته تخم مرغ / Fe_3O_4 به عنوان یک کاتالیزور ناهمگن بسیار کارآمد ساخته شده است. کاتالیست توسط طیف سنجی مادون قرمز فوریه (FT-IR)، میکروسکوپ الکترونی روبشی نشر میدانی (FE-SEM)، تجزیه پراش اشعه (XRD) و اندازه گیری خواص مغناطیسی (VSM) مشخص و تایید شد.
