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Synthesis of Fe_3O_4/Eggshell Nanocomposite and Application for Preparation of Tetrahydrobenzo[b]Pyran Derivatives

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A B S T R A C T

This work is reported on the synthesis of Fe_3O_4/eggshell nanocomposites in the absence of any stabilizer or surfactant.Fe_3O_4 magnetic nanoparticles were established on the egg shell nano-composite. The nanocompositeshave 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 dimedonewith excellent yields in the presence of Fe_3O_4/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 productshave attracted significant attention from thepoint ofview of ideal synthesis [1]. The first MCR was initiatedby Strecker in 1850 for the synthesis of amino acids [2] However, in past decades there was greatdevelopments in MCRsand significant efforts were made tofind 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-cyanocinnamonitrile 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], $H_6P_2W_{12}O_{62}\cdot H_2O$ [21], tetrabutylammonium bromide [22], cerium(III) chloride [23].However, each of the above-mentioned method 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 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 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 have 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 separationbecause 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 nanocompositepossessed 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 (Cu Kα = 1.5406 A°). The scanning rate was 2º/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 BrukerAvance DRX 400 MHz instrument. The spectra were measured in DMSO-d6 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 ºC 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 $FeCl_3.6H_2O$ (11.68 g) and $FeCl_2.4H_2O$ (4.30 g) in 200 mL deionized water. This solution was stirred with magnetic stirrer (2000 rpm) at 50 ºC for 1 h. Nitrogen gas was continuously bubbled through this solution for theremoval 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 ºC 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 2θ=29.5 and other peaks were observed at 2θ=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 2θ = 36.1°, 43.7°, 54.6°, 58.1° 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 (λ=1.54A0), 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.

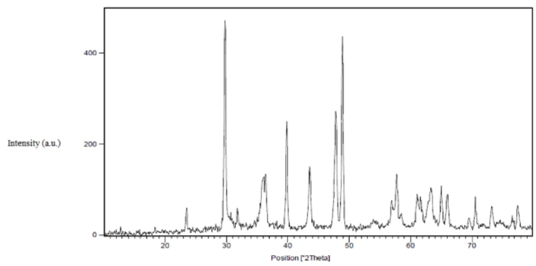


Figure 1.XRD pattern of the Fe_3O_4/eggshell Catalyst.

The magnetic properties of Fe_3O_4/eggshell were characterized by a vibrating sample magnetometer (VSM). The saturation magnetization of Fe_3O_4 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 Fe_3O_4/eggshell is 65.5 emu g^{-1}, the catalyst can be efficiently separated from the solution with an external magnetic force.

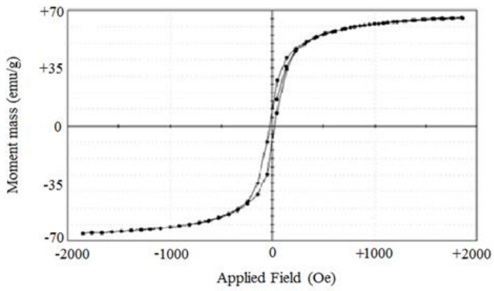


Figure 2. VSM Curve for Fe_3O_4/eggshell at room temperature.

FT-IR analysis of Fe_3O_4/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 CO_3^{2-} molecules.The absorption bands situated at 3000–2500 cm^{-1} marked with asterisks in spectrum were also attributed to organic matter[53], The peakscentered around 3400 cm^{-1} and 1620 cm^{-1} are, respectively, assigned to the O-H stretching and deforming vibrations of Fe_3O_4 and the peak at 578 cm^{-1} are corresponding to the Fe-O vibration.

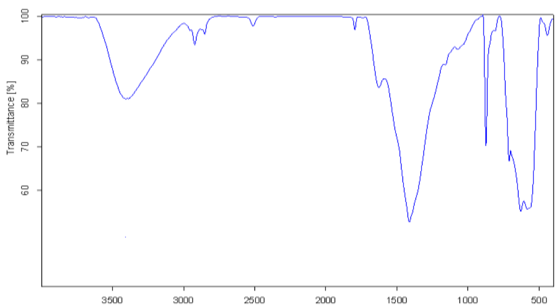


Figure 3. FT-IR Spectra of Fe_3O_4/eggshell.

The morphology of the sample was investigated with scanning electron microscopy (SEM). Figure 4 shows spherical structure Fe_3O_4/eggshell catalyst.

Optimization for the catalyst synthesis

In order to optimize the reaction conditions, the reaction of benzaldehyde (1 mmol), malononitrile (1 mmol), and dimedone (1 mmol) were carefully investigated. Tables 1 and 2 summarized the different ratio of solvent (H_2O, 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 H_2O-EtOH (1:1).

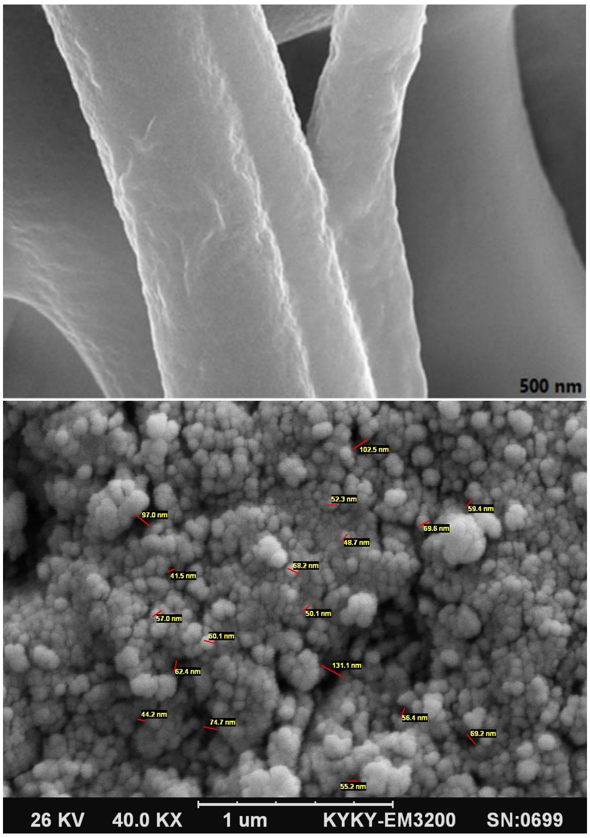


Figure 4. TEM & SEM Images of Fe_3O_4/eggshell.

TABLE 1. Effect of amount of catalyst on synthesis

Entry	Solvent	Time(min)	Yield(%)[b]
1	H_2O	120	45
2	EtOH	80	65
3	EtOH/H_2O (1/2)	60	70
4	EtOH/H_2O (2/1)	50	80
5	EtOH/H_2O (1/1)	40	98

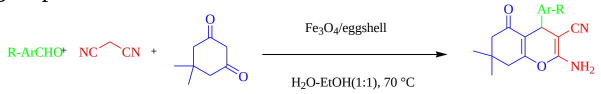
[a]Reaction conditions: 2,4 di-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), and catalyst at 70 °C.
[b]Yields refer to isolated pure product.

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

[a]Reaction conditions: 2,4 di-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), and catalyst at 70 °C.
[b]Yields 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 goodyields. The aromatic aldehydebearing electron-donating group such as OMe, reacted muchslower with malononitrile and dimedone than other aromatic aldehydessubstituted with electron withdrawing groups such as NO_2^- and Cl^-.



1 2 3

R=H, 4-MeO, 4-NO$_2$, 3-NO$_2$, 2,4 di-Cl, 4-Cl

Figure 5. Single step synthesis of 4*H*-drobenzo[*b*]pyran derivatives catalyzed by Fe_3O_4/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 H_2O-EtOH (1:1) at 70 °C.

Entry	Ar	Time (min)	Yield(%)
1	C_6H_5	50	80
2	4-MeOC_6H_4	70	75
3	3-NO$_2$$C_6H_4$	30	92
4	4-NO$_2$$C_6H_4$	25	98
5	2,4-ClC_6H_3	30	92
6	4-ClC_6H_4	40	90

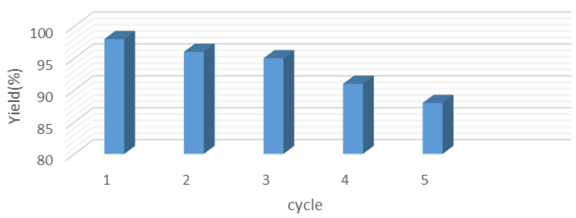


Figure 6. Reusability of catalyst. Reaction conditions: 2,4 di-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), dimedone and Fe_3O_4/eggshell (50 mg) at 70°C.

After the reaction was completed, the catalyst was recovered using an external magnet, and in order to be reused. The reused catalyst was washedwith ethanol for several times and then dried. The catalyst showed no significant lossesin 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 Fe_3O_4/eggshell at mild conditions. The catalyst is completely recoverable due to the superparamagnetic behavior of Fe_3O_4 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 اسیدیته نانوکامپوزیت پوسته تخم مرغ ایجاد شده است. این نانوکامپوزیت‌ها، 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 نانوکامپوزیت 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 اندازه‌گیری خواص مغناطیسی (VSM) مشخص و تایید شد.