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Research article

Fe_3O_4 nanoparticles impregnated eggshell as an efficient biocatalyst for eco-friendly synthesis of 2-amino thiophene derivatives

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A R T I C L E I N F O

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A B S T R A C T

In this study, a biodegradable and eco-friendly biocatalyst (eggshell/Fe_3O_4) was synthesized utilizing eggshell impregnated with Fe_3O_4 nanoparticles. The characterization of prepared catalyst was carried out by Fourier transform infrared radiation (FT-IR), scanning electron microscopy (SEM), X-ray Diffraction (XRD), energy-dispersive X-ray (EDX), thermal gravimetric analysis-differential thermogravimetry (TGA-DTG), vibrating sample magnometer (VSM), and atomic force microscopy (AFM). The eggshell/Fe_3O_4 biocatalyst was served in multi-component reactions (MCRs) for the synthesis of 2-amino thiophene derivatives from variety aromatic aldehydes, malononitrile, ethyl acetoacetate, and sulfur (S8). To achieve optimal reaction conditions, a thorough examination was conducted on key factors, such as the solvent type, reaction time and temperature, and the ratio of eggshell to Fe_3O_4. The findings suggest that high yield product can be obtained at microwave temperature (MW) in EtOH solvent within 10 min. Additionally, the eggshell/Fe_3O_4 biocatalyst exhibited high catalytic activity, which was sustained over the five cycles, without any significant decline in its performance.

1. 1- Introduction

Recently, the attention has been concentrated on some eco-friendly and economically sustainable procedures for the synthesis of organic compounds with high yield products. Eggshell wastes are abundant and cheap biomaterials, which are mainly consist of calcium carbonate (main principle), acid amines, uronic acid, proteins, carbohydrates, and lipids [1–3]. Regarding these intriguing ingredients, the eggshell may be deemed a green catalyst in some organic syntheses that require a fundamental catalyst [4,5]. Moreover, the magnetic nanoparticles have been widely used in some new important chemistry reactions, including drug delivery, magnetic resonance imaging, hyperthermia cancer treatment, and bio separation [6,7]. In this study, the objective was to enhance the magnetic characteristics of the produced nanocomposite by incorporating Fe_3O_4 nanoparticles into the eggshell matrix. 2-amino thiophene derivatives belong to a noteworthy category of organic compounds, constituting the main constituents of natural products [8–10]. Today, aminothiophene derivatives are used in many applications, including pesticides, dyes, and pharmaceuticals. These are heterocyclic five-membered building blocks that occur naturally or can be synthesized organically. In addition to being easily

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accessible, thiophene is chemically stable, and its chemistry is being studied in current research. Its diverse properties include its ability to be antimicrobial, anticancer, anti-inflammatory, anti-psychotic, anti-arrhythmic, anti-anxiety, and many more [11–14]. Due to the aforementioned applications and the significance of these compounds, a variety of versatile methods under different conditions have been reported for the synthesis of 2-amino thiophene derivatives, Gwald [15,16], Heinsberg [17], paal-Knorr [18], and Fiesselmann [19] thiophene syntheses. Among them, Gwald aminothiophene synthesis is a well-established approach that is employed for the production of a wide range of 2-aminothiophene derivatives [20]. One of the most commonly of these methods is the using different catalysts, including metal oxides (such as Fe_3O_4), chemical indicators, organic bases, and ionic liquids by condensation of aldehyde, malononitrile, and 1,3-dicarbonyl compounds [21,22]. Nevertheless, these techniques present numerous drawbacks, comprising exorbitant expenses, severe reaction conditions, inferior efficiency, extended reaction time, and hazardous solvent. The heightened focus on safeguarding the environment over the past few decades has prompted contemporary academic and industrial communities to develop chemical procedures that optimize output and minimize expenses. The multi-component reaction (MCR) strategy is an efficient tool utilized to combine economic and environmental aspects. This approach comprises multiple synthetic steps that are performed without isolating intermediates, thereby curtailing time and conserving resources such as money, energy, and raw materials [23–30]. Herein, we synthesized 2-amino thiophene derivatives in the presence of eggshell/Fe_3O_4 as an efficient biocatalyst under mild reaction conditions. The novelty of this study lies in the fact that the eggshell/Fe_3O_4 biocatalyst has not been employed for synthesizing 2-amino thiophene derivatives and the outcomes and efficacy have not been documented.Various crucial factors of the model reaction, including the dosage of the catalyst, the specific type of solvent employed, the reaction temperature, as well as the recovery process of the catalyst, were also thoroughly examined. The as-prepared biocatalyst displayed significant advantages, such as excellent efficiency, short reaction time, and catalyst recyclability.

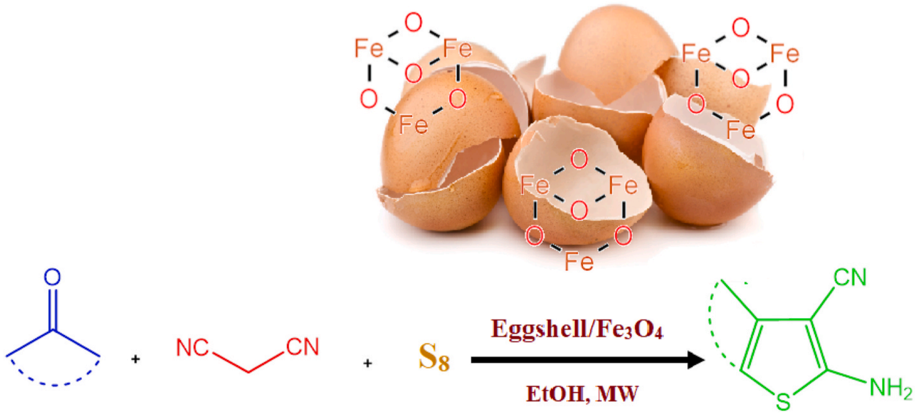
2. Experimental section

2.1. Preparation of magnetic eggshells nanocomposite (eggshell/Fe_3O_4)

At the outset, the collection of eggshells was followed by their immersion in a NaOH solution (0.5 M), and subsequent boiling for 60 min. After that, the corresponding eggshells washed several times with deionized water and dried at 800 °C in an oven for 24 h. As a consequence of these procedures, the resultant particles were obtained with a dimension of 75–150 μm. A co-precipitation method was employed in order to synthesize magnetic nanoparticles. Following this, 0.04 mol of $FeCl_3 \cdot 6H_2O$ and 0.02 mol of $FeCl_2 \cdot 4H_2O$ was dissolved in 50 mL of distilled water. Subsequently, NaOH solution (1.5 M) and prepared magnetic solution of eggshell were incrementally introduced to the mixture at a temperature of 60 °C under a N_2 atmosphere. The reaction temperature was further increased to 80 °C for 1 h. Consequently, the resulting product (denoted as eggshell/Fe_3O_4) was washed with deionized water, and subsequently dried under vacuum for 12 h [31].

2.2. Synthesis of 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile

A solution of cyclohexane (1 mmol), malononitrile (1 mmol), sulfur (S8) (1 mmol), eggshell/Fe_3O_4 biocatalyst (0.03 g), and EtOH (3 mL) was initially stirred under microwave conditions (Scheme 1). The reaction was monitored by TLC (n-hexane, EtOAc, 3:1) method. After completion of the reaction, the mixture was cooled to produce pure crystal structure. Finally, the resultant product was collected and dried after recrystallization by 3 mL of EtOH. To achieve the most optimized ratio, eggshell/Fe_3O_4 nanocomposites were prepared in different concentrations of eggshell to Fe_3O_4. Finally, the best ratio of eggshell and Fe_3O_4 was determined (Table 1). In the following, to study the catalytic performance of prepared nanocomposite, the three-component reaction of benzaldehyde, malononitrile, ethyl acetoacetate, and sulfur was considered as a model reaction. The eggshell/Fe_3O_4 biocatalyst with a concentration of 5:1



Scheme 1. Synthesis of 2-amino thiophene derivatives catalyzed with eggshell/Fe_3O_4 biocatalyst through multi-component reaction between aromatic aldehydes, malononitrile, ethyl acetoacetate, and sulfur (S8) in EtOH solvent at MW temperature.

Table 1
Different ratios between eggshell and Fe_3O_4 nanoparticles.

Entry	Ratio (eggshell: Fe_3O_4)	Time (min)	Yield (%)
1	1:1	120	51
2	5:1	10	96
3	0.5:1	Just intermediate is formed	–
4	4:1	60	74

was utilized in the synthesis of 2-amino thiophene derivatives. Calcium carbonate ($CaCO_3$) is the main component of eggshell, inducing an alkaline environment. The detection of Fe_3O_4 was accomplished without resorting to additional external bases. To determine the effect of reaction time (t), different component was separately used in the model reaction and the results are summarized in Table 2. The product was synthesized in the presence of eggshell/Fe_3O_4, yielding the highest amount and requiring the least amount of time, as indicated in Table 2.

2.3. Characterization methods

The Fourier transform infrared radiation (FT-IR) spectra of samples reported in solid state utilizing KBr pellets with FT-IR spectrometer (BRUKER OPTICS Co, GER) from 400 to 4000 cm^{-1}. The X-ray Diffraction (XRD) patterns were determined using Cu Ka radiation (k = 1.542A) with the Bragg angle ranging from 10° to 80° (RigakuD-Max). Moreover, Vibrating Sample Magnetometer (VSM) analysis was investigated by Magnates Daneshpaghoh Co, Kashan, Iran. The morphology, crystal structure, and chemical characterization were evaluated *via* an emission scanning electron microscope along with an energy-dispersive X-ray (EDX) (SEM, Hitachi S-4800, Japan). In addition, a simultaneous analyses of thermal gravimetric analysis-differential thermogravimetry (TGA-DTG) were conducted on a NETZSCH STA 409 PC/PG Germany spectrometer. Furthermore, AFM analysis (Bio-AFM Opaque Kit) was used to measure the height and elevation of the surfaces (topography) and two and three-dimensional imaging of the surfaces.

3. Results and discussion

3.1. Characterization of Eggshell/Fe_3O_4 magnetic nanocomposite

3.1.1. IR adsorption analysis

As can be seen in Fig. 1a the peak appeared at 570 cm^{-1} is related to characteristic absorption band of Fe–O vibrations. According to FT-IR analysis of eggshell/Fe_3O_4 (Fig. 1b), the peaks at 2505 cm^{-1} (HCO_3), 1795 cm^{-1} (CO), 1421 cm^{-1} (C–O), 876 cm^{-1} (O–C–O), and 709 cm^{-1}(C–O) are related to carbonate absorptions [32]. The characteristic band at 588 and 3414 cm^{-1} are associated to stretching vibrations of Fe–*O*–Fe and OH groups present in $Ca(OH)_2$ [33]. These vibrations are attributed to the adsorption of water on the surface of the eggshell/Fe_3O_4 magnetic nanocomposite.

3.1.2. TGA-DTG analysis

The thermal stability of the eggshell/Fe_3O_4 biocatalyst was examined through the use of TGA-DTG, which was conducted over the temperature range of room temperature to 900 °C (Fig. 2). The primary reduction in weight (1.98 %) is linked to the decomposition of eggshell into CaO and CO_2, which substantiates the presence of carbonate within the eggshell framework [34]. Moreover, the $CaCO_3$ of the eggshell was seen to be thermally stable up to 600 °C. The decomposition of the composite occurred from 600 to 700 °C seen here as total percentage mass loss of 12.97 %. This mass loss occurred due to loss in water content and organic matter from the eggshell. Beyond the temperature of 600 °C, an abrupt decrease in weight is observed. This phenomenon validates the conversion of $CaCO_3$ to CaO by the liberation of CO_2.

3.1.3. Morphological observation

The SEM image of the Fe_3O_4 nanoparticles indicate that the prepared nanoparticles have spherical shape and uniform size (Fig. 3a). Furthermore, it can be observed that the surface of the eggshell is fully encapsulated by the magnetic Fe_3O_4 particles, which exhibit a spherical morphology (Fig. 3b) [35]. Furthermore, the SEM images provide evidence that the Fe_3O_4 nanoparticles possess an average diameter of approximately 76 nm. The distribution of Fe_3O_4 nanoparticles on the porous surface of the eggshell is well-balanced, resulting in a nanocomposite with a significantly large surface area. Consequently, this nanocomposite material holds promising potential as an effective catalyst for various chemical reactions. The histogram pertaining to the distribution of particle sizes is

Table 2
Effect of time on reaction yield with different precursors.

Entry	Catalyst	Time (min)	Yield (%)
1	eggshell/Fe_3O_4	10	96
2	eggshell	180	90
3	eggshell + Fe_3O_4	180	85
4	Fe_3O_4	240	60

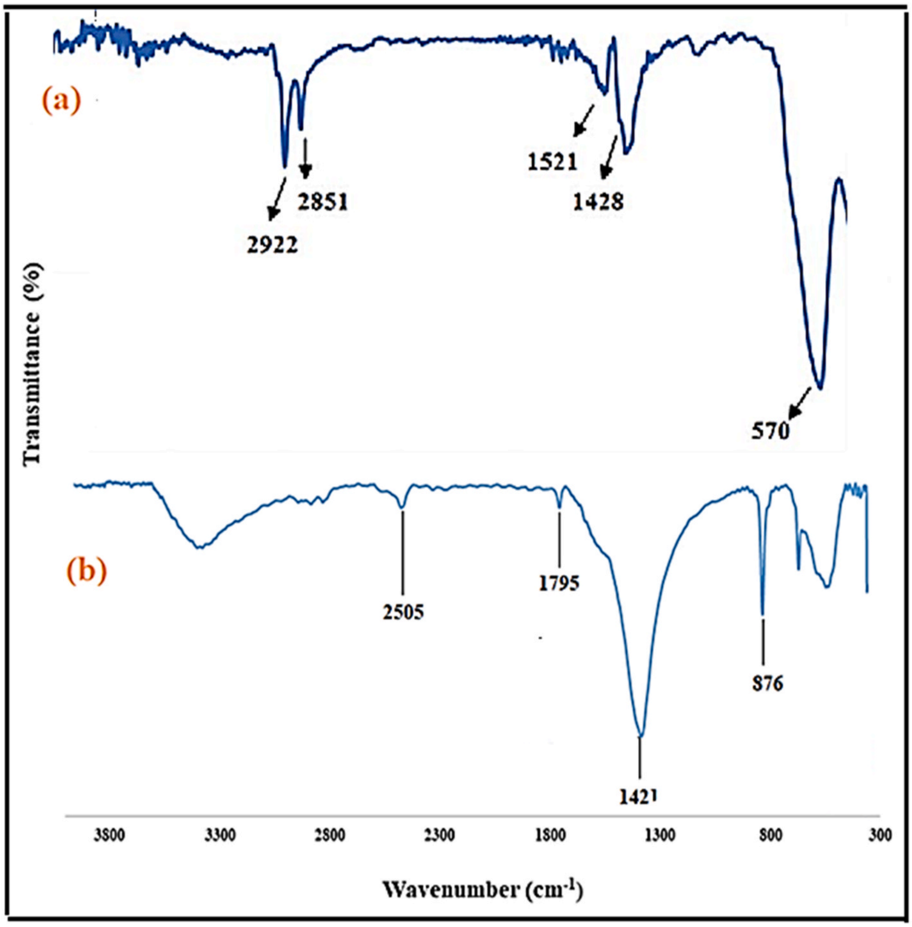


Fig. 1. FT-IR spectra of (a) Fe_3O_4 nanoparticles and (b) eggshell/Fe_3O_4 magnetic nanocomposite.

observable within Fig. 3d. Derived from the acquired outcomes, it can be inferred that over 80 % of the particle sizes exist within the range of 70–100 nm.

3.1.4. XRD data

Fig. 4 exhibits the XRD pattern of the eggshell/Fe_3O_4 catalyst, whereby the predominant peak is observed at 2θ = 29.5. Furthermore, several other peaks are discernible at 2θ = 36.2°, 40.1°, 44.2°, 48.7°, 57.7°, and 62.1°. These peaks correspond to the crystallography planes of (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 4 0), and (5 1 1). It is noteworthy that these planes can be associated with a face-centered cubic structure of $CaCO_3$ (JCPDS no. 5–0586). Additionally, the XRD pattern of the eggshell/Fe_3O_4 catalyst demonstrates diffraction peaks at 2θ = 36.1°, 43.7°, 54.6°, 58.1°, and 61.4°, which can be attributed to the diffraction of the (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) planes of the cubic phase Fe_3O_4. As demonstrated by the XRD patterns depicted in Fig. 4, the dominant peak observed at an angle of 2Θ = 34° corresponds to the eggshell phase [36]. The crystal size of the resulting nanocomposite particles was estimated to be 76.4 nm using the Debye-Scherrer equation [37–43].

3.1.5. VSM analysis

An image of the VSM showing the eggshell/Fe_3O_4 biocomposite can be observed in Fig. 5. The magnetic characteristics of this nanocomposite can be determined by examining its magnetic hysteresis curve. It is expected that the impressive magnetic properties exhibited by the Fe_3O_4 nanoparticles will be diminished when they are combined with the eggshell component. Nevertheless, the saturation magnetization of the eggshell/Fe_3O_4 nanocomposite is found to be 13 emu.g^{-1}, thereby confirming its inherent magnetic nature. As a result, the as-prepared biocatalyst can be easily separated from the reaction mixture by utilizing an external magnetic field.

3.1.6. AFM analysis

AFM is one of the prototype devices for producing two-dimensional and three-dimensional (3-D) patterns and surface topography. As depicted in Figs. 6 and 7, the dimensions of length, width, height, uniform slope, atomic resolution, force atomic, and bounding are

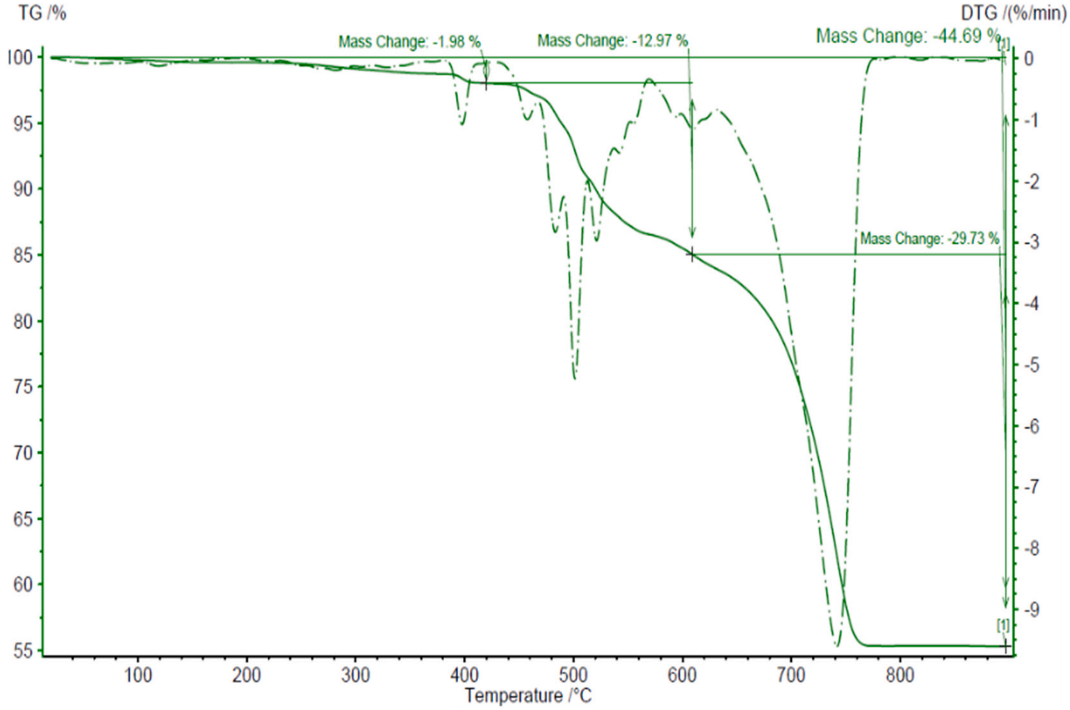


Fig. 2. TGA-DTG curve of the eggshell/Fe_3O_4 biocatalyst.

evidently exhibited on the surface of the synthesized nanocomposite. In the 2-D pattern depicted in Fig. 6, the measurements of length and width are 10 nm, while the height is 0.057 nm. Conversely, in the 3-D pattern displayed in Fig. 7, the length and width are defined as 18 nm. Moreover, the adhesion and cohesive forces between atoms are consistently indicated.

3.1.7. EDAX analysis

Fig. 8 depicts a representative EDAX pattern of the eggshell/Fe_3O_4 nanocomposite. The EDAX pattern exhibits six distinct peaks, which correspond to various elements, including Ca, C, O, and Fe in the structure of nanocatalyst. Notably, the amounts of Ca and C surpass that of Fe and it corresponds to the ratio of eggshell to Fe_3O_4)5:1 (. This distinction is discernible based on the differing magnitudes of the highest peaks in Fig. 8.

3.2. Catalytic results of eggshell/Fe_3O_4 for synthesis of 2-amino thiophene derivatives

The catalytic activity of eggshell/Fe_3O_4 was considered in the synthesis of 2-aminothiophene derivatives. Therefore, in order to achieve the optimal conditions for the formation of 2-aminothiophene, the three-component interaction involving cyclohexane, malononitrile, and sulfur (1:1:1 M ratio) was employed as a representative reaction. The outcomes of this experiment are presented in Tables 3 and 4. To evaluate the optimal value of reaction parameters, a variety of parameters, including the amount of biocatalyst, type of solvent, reaction time and temperature were discussed. The progression of the reaction was regulated through the TLC chromatography. The synthesis of 2-amino-4,5,6,7-tetrahydrobenzo [b] thiophene-3-carboxylate was achieved using EtOH as the solvent, yielding the lowest efficiency (40 %) at room temperature (r.t) after 270 min (Entry 1). Moreover, it was observed that increasing the temperature had a positive impact on the product yield. Moreover, the increasing of temperature has affected on the output of the product. Additionally, the utilization of elevated temperatures (ranging from 60 to 400 °C) has been scrutinized (Entries 2 and 3), leading to a moderate influence on the reaction yield of the desired product (53 %). Furthermore, in terms of optimizing the solvent, the most favorable outcome was achieved when using ethanol (Entry 11). Conversely, under solvent-free conditions, no product was obtained, while by CH_2Cl_2 resulted in the longest reaction time (Entry 8). Subsequently, the final investigation revolved around the implementation of microwave (MW) conditions at varying reaction times. There was no discernible difference in yield between EtOH and water under MW conditions, despite their differing reaction times. Therefore, EtOH was established as the optimal eco-friendly solvent for all derivatives of 2-amino thiophene, as demonstrated by thorough experimentation (Entries 15 and 16). It is noteworthy that the utilization of Me_3CN and CH_2Cl_2 as aprotic solvents in MW conditions did not significantly impact the yield or reaction time (Entries 5 and 6). Ultimately, Me_3CN and CH_2Cl_2 solvents yielded lower reaction efficiencies and longer reaction times compared to water and EtOH as protic solvents (Entries 9 and 11).

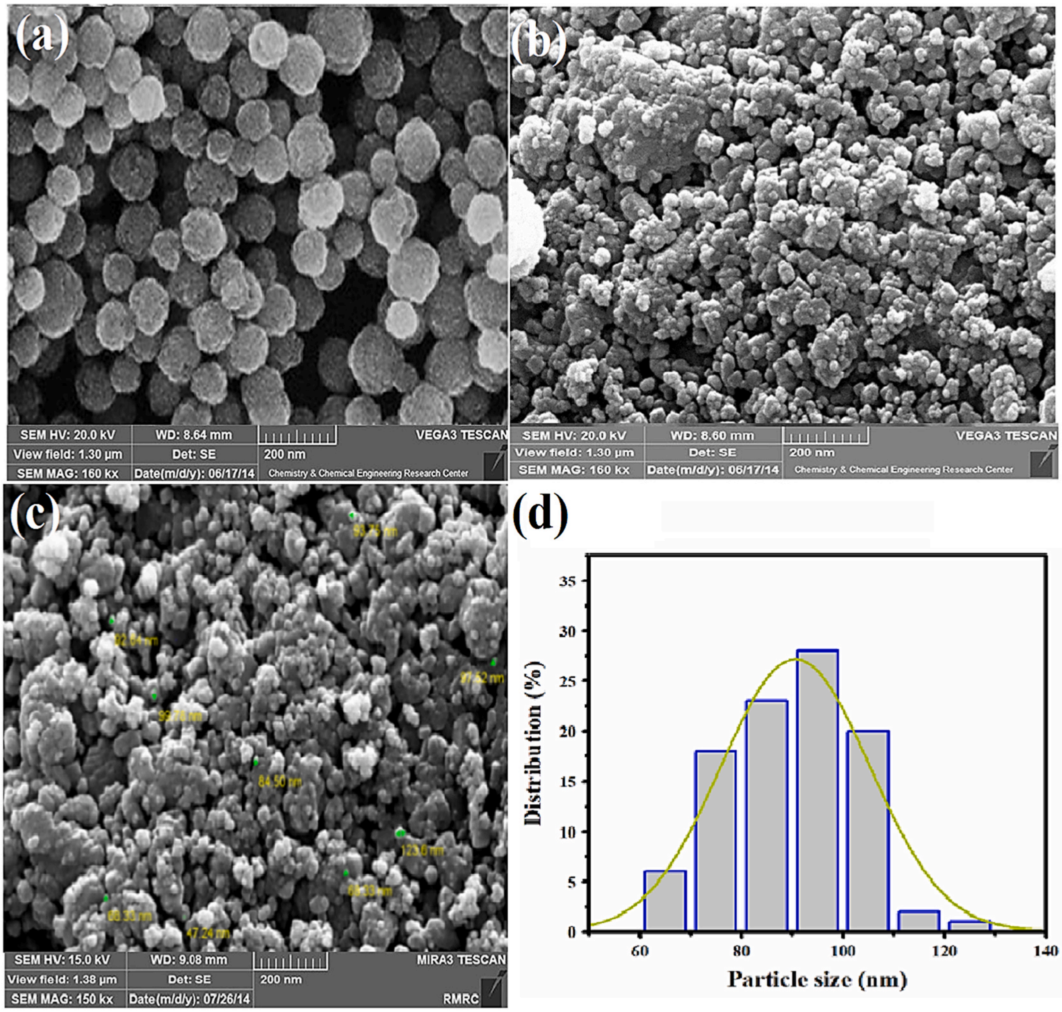


Fig. 3. The SEM images of (a) Fe_3O_4 nanoparticles, (b,c) eggshell/Fe_3O_4 biocatalyst, and (d) the particle sizes distribution of the eggshell/Fe_3O_4.

3.3. Development of optimal conditions for synthesizing other derivatives of 2-amino thiophene

After the optimization of the reaction conditions for the synthesis of other derivatives of 2-amino thiophene, we proceeded to investigate this reaction using a diverse range of ketones, sulfur (S8), and nitrile compounds (Table 5). Here, we present an effective procedure for the synthesis of 2-amino thiophenes derivatives (Entry 1-1a) through a three-component condensation reaction involving ketones (1 mmol), nitrile compounds, and sulfur (S8), with the utilization of eggshell/Fe_3O_4 as a reusable, non-toxic, and eco-friendly catalyst under microwave conditions. However, when aromatic ketones were employed, the reactivity of the carbonite functional group was observed to decrease due to the resonance effect between the carbonite and aromatic ring (Entries 1-2a). In the case of Entry 4-4a, the enolate form was successfully generated, resulting in a shorter reaction time compared to entry 3-3a. Furthermore, the presence of cyclohexane led to the formation of various conformations, thereby affecting the reaction time difference between (Entries 5-5a and 6-6a). The reaction time was increased due to the induction effect of the halogenide on the aromatic ring in (4-Br)-acetophenone (Entry 9-9a). Notably, the strict effect was observed in the subsequent entries 10-10a and 11-11a. Finally, in entries 12-12a and 14-14a, the ring size and induction effects contributed to the production of various products, albeit with minor differences in their outcomes.

3.4. Proposed pathway of the reaction mechanism

The Gwald mechanism was determined in accordance with Scheme 2, which outlined the key steps of the one-pot three component reaction in the presence of the alkali eggshell/Fe_3O_4 catalyst nanocomposite. Fe_3O_4 nanomaterials were synthesized and were loaded in eggshell for better recovery of the catalyst after synthesis of 2-amino thiophene derivatives. Initially, a Knoevenagel condensation occurred between ketones and α-cyano ester, resulting in the formation of intermediate (I). Subsequently, sulfur (S8) was introduced to

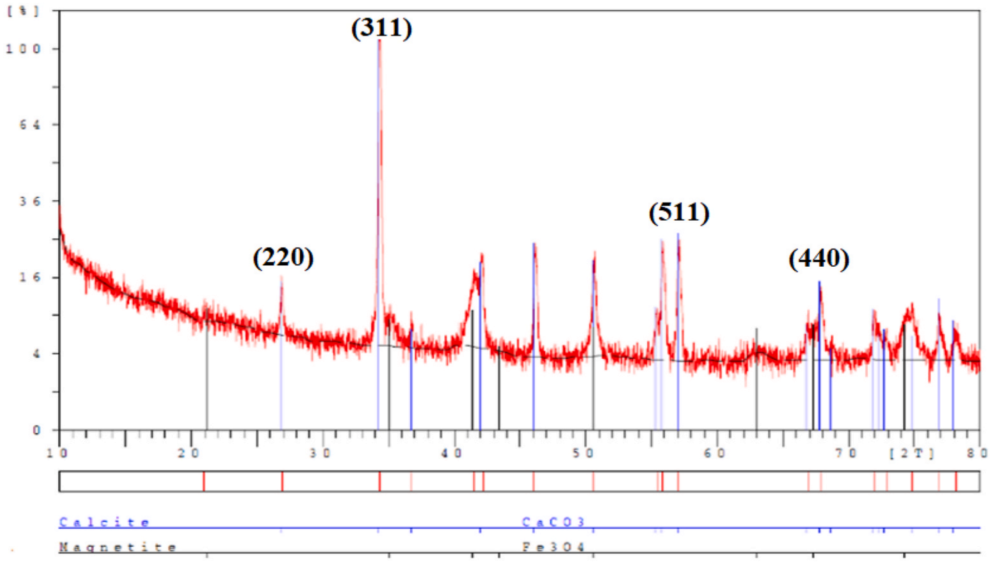


Fig. 4. XRD pattern of the eggshell/Fe_3O_4 magnetic biocatalyst.

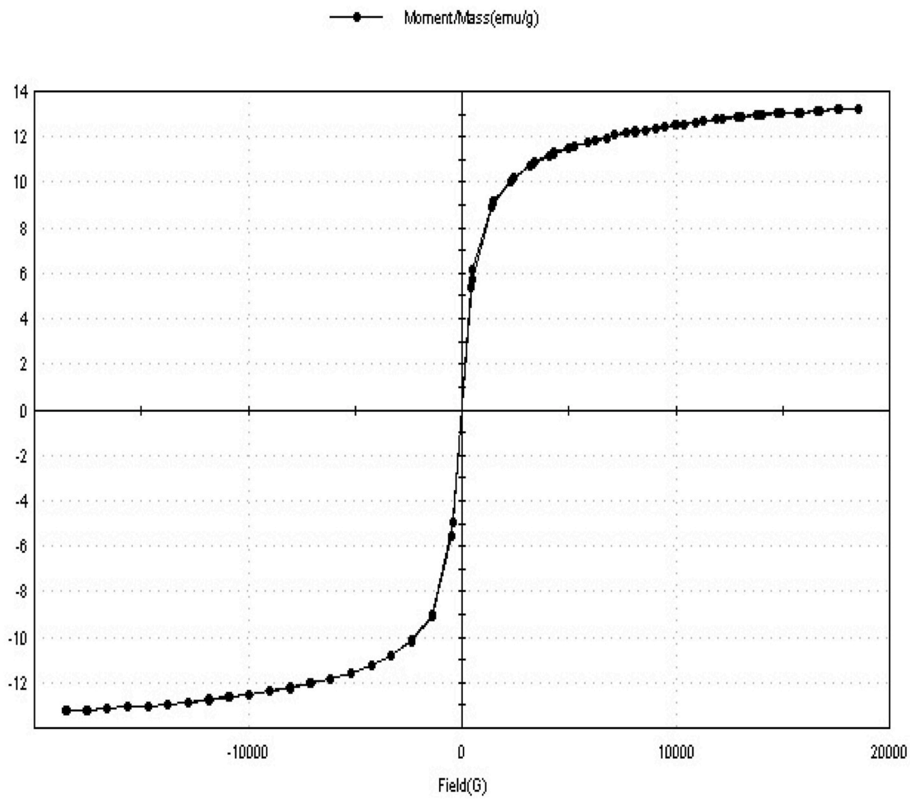


Fig. 5. VSM analysis of eggshell/Fe_3O_4 magnetic nanocomposite.

induce the sulfur product. Finally, the tautomerization of the intermediate led to the closure of the major ring of 2-amino thiophene, yielding the final product. The presence of ethanol played a role in generating a stable intermediate by forming a hydrogen bond with the oxygen of the carbonyl functional group in ketones. Eggshell/Fe_3O_4 biocatalyst plays a crucial role in regulating the specificity of the reaction, thereby exerting an influence on the formation of specific products.

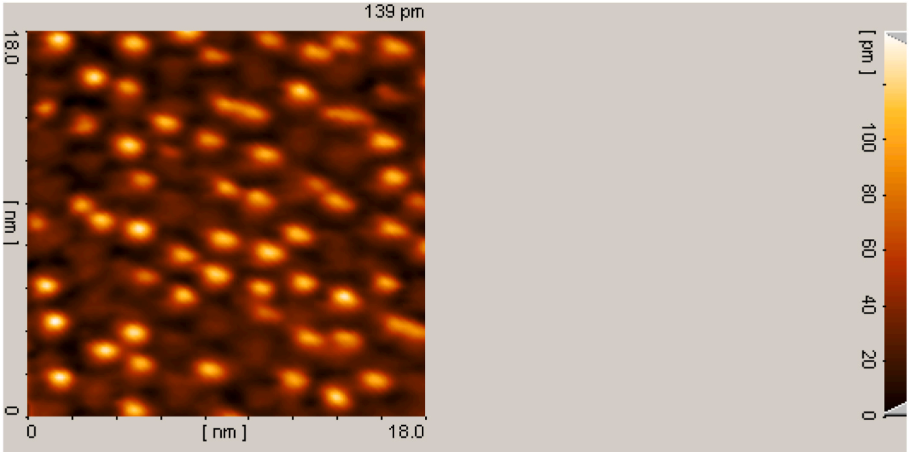


Fig. 6. (2-D) AFM pattern of eggshell/Fe_3O_4 biocatalyst.

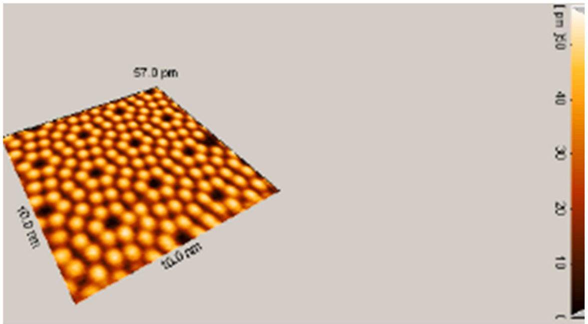


Fig. 7. (3-D) AFM pattern of eggshell/Fe_3O_4 biocatalyst.

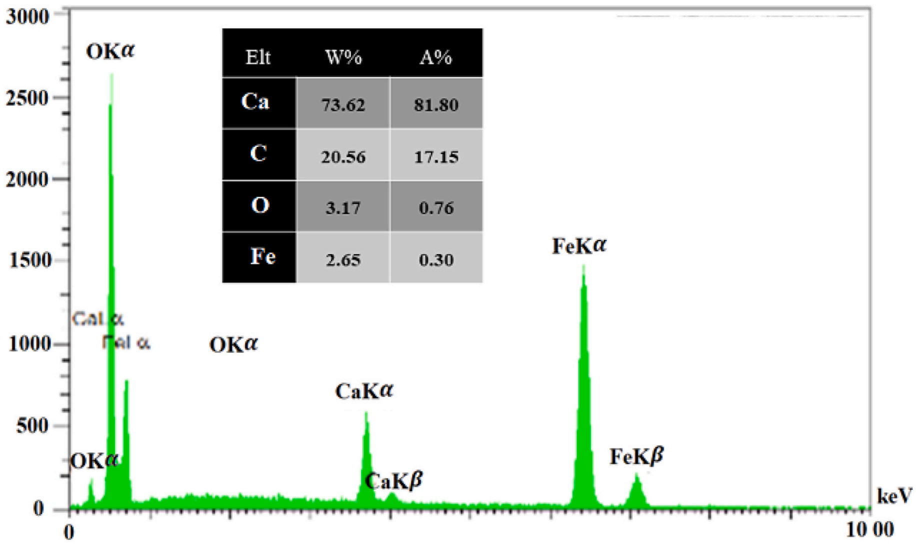


Fig. 8. EDAX analysis of the eggshell/Fe_3O_4 nanocomposite.

Table 3
Optimizing the reaction conditions of catalyzed by Eggshell/Fe_3O_4 biocatalyst[a].

Entry	Loading (mg)	Solvent	Condition	Time (min)	Yield (%)
1	10	H_2O	MW	45	56
2	20	H_2O	MW	36	78
3	30	H_2O	MW	5	89
4	40	H_2O	MW	5	89

[a] The reaction of cyclohexanone (a), and malononitrile(b) and sulfur (S8), (molar ratio 1:1:1) as a model reaction.

Table 4
One pot three component reaction of variety aromatic ketone, malononitrile, and sulfur *via* eggshell/Fe_3O_4 (30 mg).

Entry	Catalyst	Loading (mg)	Solvent	Temp (°c)	Time (min)	Yield (%)
Optimizing of temperature						
1	Eggshell/Fe_3O_4	30	EtOH	r.t	270	40
2	Eggshell/Fe_3O_4	30	EtOH	40	200	50
3	Eggshell/Fe_3O_4	30	EtOH	60	150	53
4	Eggshell/Fe_3O_4	30	EtOH	Reflux	10	96
5	Eggshell/Fe_3O_4	30	EtOH	MW,60	20	89
6	Eggshell/Fe_3O_4	30	EtOH	MW,80	5	89
Optimizing of solvent						
7	Eggshell/Fe_3O_4	30	CH_3CN	MW	120	50
8	Eggshell/Fe_3O_4	30	CH_2Cl_2	MW	150	>50
9	Eggshell/Fe_3O_4	30	H_2O	MW	20	89
10	Eggshell/Fe_3O_4	30	–	MW	>120	–
11	Eggshell/Fe_3O_4	30	EtOH	MW	5	89
Optimizing of time						
12	Eggshell/Fe_3O_4	30	EtOH	MW	2	<50
13	Eggshell/Fe_3O_4	30	EtOH	MW	3	55
14	Eggshell/Fe_3O_4	30	EtOH	MW	4	62
15	Eggshell/Fe_3O_4	30	EtOH	MW	10	89
16	Eggshell/Fe_3O_4	30	EtOH	MW	5	89

3.5. Recovery and reusability of eggshell/Fe_3O_4 biocatalyst

Due to evaluate the reusability of the eggshell/Fe_3O_4 biocatalyst, the synthesized catalyst was separated by centrifugation and washed with water several times. The observations portrayed in Table 6 demonstrate a gradual decrease for the synthesize of 2-amino thiophene derivatives from 89 % to 83 % throughout five successive iterations. As a result, it is plausible to affirm that eggshell/Fe_3O_4 biocatalyst is a proficient and reusable nanomaterial that can be utilized effectively for the synthesis of 2-amino thiophene derivatives. The little reduction in the efficiency of the biocatalyst following the fifth restoration cycle could potentially be attributed to the insufficient occupancy of the catalytic sites by either substrates or reaction products. Moreover, the XRD results for eggshell/Fe_3O_4 biocatalyst after each recovery are presented in Fig. 9. The XRD analysis was conducted on the retrieved nanocatalyst to assess the stability of its structure. It was observed that there were no changes in the position of the peaks or in the structure of eggshell/Fe_3O_4 after undergoing five cycles.

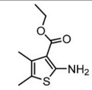
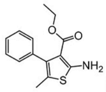
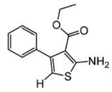
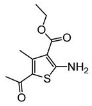
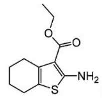
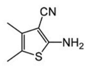
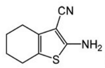
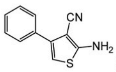
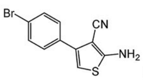
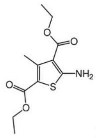
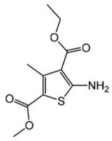
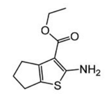
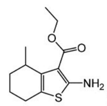
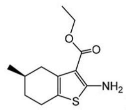
4. Conclusions

In the current investigation, to synthesize of 2-amino thiophene derivatives, which belong to a significant category of organic compounds, was carried out. For this, eggshell/Fe_3O_4 magnetic nanocomposite derived from a natural origin, was employed under eco-friendly and sustainable conditions. The advantages of this method include the presence of a green and biodegradable catalyst, the recovery of the catalyst, and the simplicity of the work up process, which results in high yields products. In all instances, the corresponding 2-amino thiophene derivatives were synthesized with high efficiency, a short reaction time (10 min), a straightforward work up procedure, no requirement for column-chromatography, eco-friendly, and cost-effective catalyst. Moreover, the eggshell/Fe_3O_4 biocatalyst was able to be reused multiple times without a significant decrease in yield percentages. Overall, this particular area of study provided a remarkable illustration of catalytic behavior and was formulated as a potentially appealing heterogeneous catalyst for the synthesis of 2-amino thiophene derivatives.

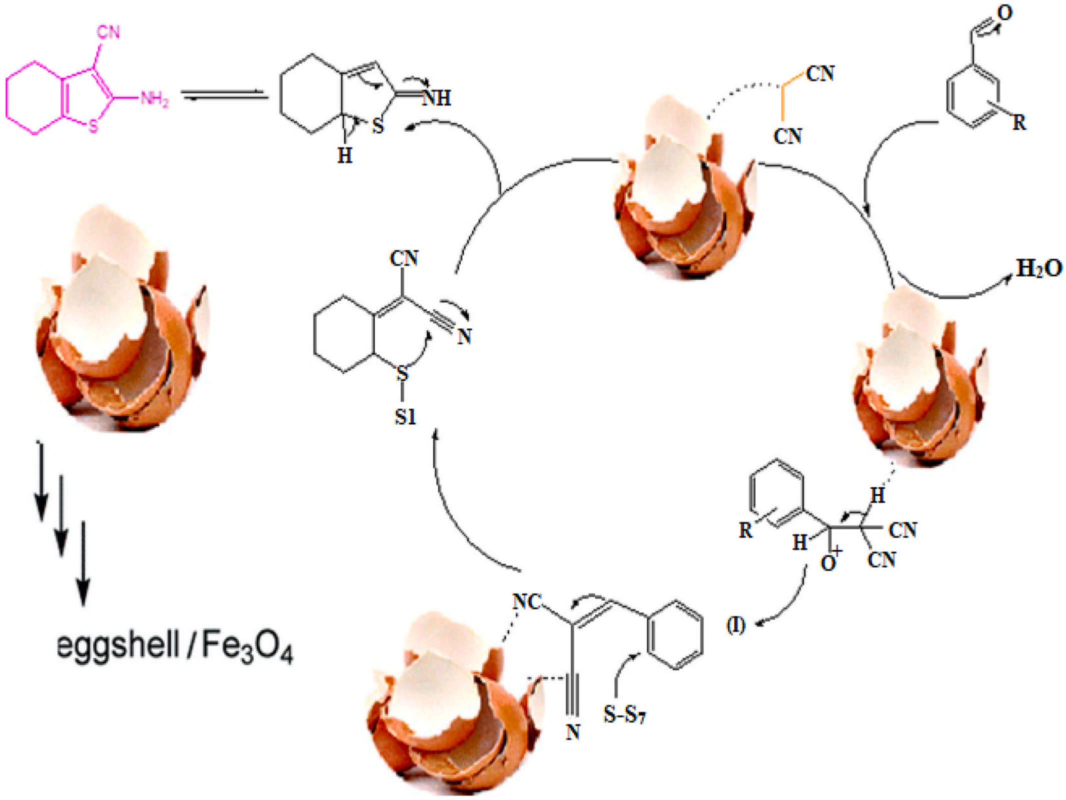
Data availability

Data will be made available on request.

Table 5
Synthesis of 2-amino-4,5,6,7-tetrahydrobenzo [b] thiophene-3-carboxylate derivatives *via* condensation of ketones, malononitrile, ethyl cyanoacetate, and sulfur (S8) in the presence of Eggshell/Fe_3O_4 biocatalyst[a] [44,45].

Entry	ketones (1)	Nitrile compounds (2)	Product	Time (min)	Yield (%)	M.p. Observed-[ref]
1			 1a	4	95	91-100 [44]
2			 2a	5	97	93-102 [44]
3			 3a	6	93	98-105 [44]
4			 4a	4	90	161-170 [44]
5			 5a	5	93	115-123 [44]
6			 6a	4	94	141-150 [44]
7			 7a	5	89	139-147 [44]
8			 8a	4	90	142-150 [44]
9			 9a	7	88	190-203 [44]
10			 10a	10	90	108-110 [45]
11			 11a	10	93	115-122 [45]
12			 12a	15	82	92-102 [45]
13			 13a	12	87	112-125 [45]
14			 14a	12	87	69-82 [45]

[a] Reaction conditions: ketone 1 (1 mmol), nitrile compound 2 (1 mmol), sulfur (S8) (1 mmol), Eggshell/Fe_3O_4 (30 mg), EtOH (5 mL), Microwave.



Scheme 2. Gwald mechanism for the synthesis of 2-aminothiophene in the presence of synthesized biodegradable catalyst.

Table 6
Reuse of the as-prepared biodegradable catalyst for the synthesis of 2-amino thiophene derivatives.

Run	Isolated yield (%)
1	89
2	88
3	86
4	85
5	83

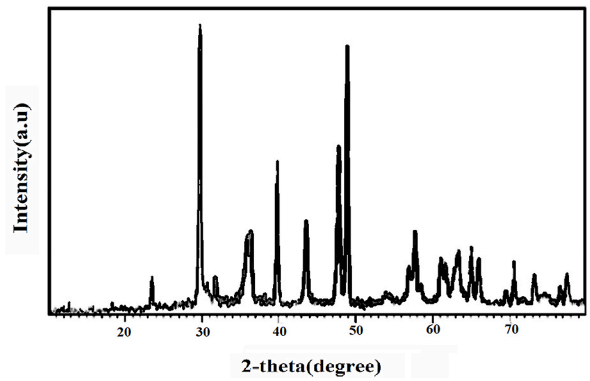


Fig. 9. XRD pattern of eggshell/Fe3O4 magnetic biocatalyst for the synthesis of *tri*-substituted derivatives of 2, 4, 5-(H1)-imidazoles after fifth recyclability.

CRediT authorship contribution statement

Mahsan Zargari: Methodology, Investigation, Formal analysis, Data curation. **Hadi Hassani Ardeshiri:** Writing – review & editing, Visualization, Software, Methodology. **Hossein Ghafuri:** Writing – review & editing, Visualization, Validation, Project administration, Conceptualization. **Maryam Mohammad Hassanzadeh:** Software, Methodology, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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