

# Design, synthesis, characterization and application of magnetic biochar as a reusable nanocatalyst for the synthesis of tetrazole derivatives

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## Abstract

Magnetic materials show promising applications in heterogeneous catalysis due to their ease of isolation and excellent reusability. Magnetic nanoparticles have emerged as a promising alternative in biosorbent modification because of their large surface area and adsorption efficiency. These adsorbents are also unique, fertile, compatible, easy to synthesize, economical, and environmentally friendly. They can also be easily extracted from mixtures obtained from adsorption processes. However, the main challenge in applying these magnetic nanoparticles is high cost when using these materials alone. This issue can be solved through combining these materials with biochar. The present study reports the design, synthesis, and characterization of a new magnetic Fe<sub>3</sub>O<sub>4</sub> biochar catalyst. The structures and properties of Magnetic biochar bis(thiourea) triazin copper (II) (MBC@BTT-Cu(II)) were fully characterized using various physicochemical techniques. The prepared catalyst showed excellent catalytic activity for the synthesis of 5-substituted 1H-tetrazole derivatives. This new method shows some important features, including high efficiency, lower catalyst loading, easy operation, and the ability to recycle the catalyst for at least six times without obvious degradation of the catalytic performance. Furthermore, MBC@BTT-Cu(II) nanocatalyst can be reused in up to five cycles without loss in catalytic activity.

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## 1. Introduction

Biomass-based materials have enormous potential as functional materials, capable of replacing traditional materials and reducing dependence on fossil resources and environmental pollution [1, 2]. Due to their abundance in nature, renewability, biodegradability, and non-toxicity, biomass materials are considered an ideal alternative for preparing heterogeneous catalysts [3-5]. These materials possess numerous attractive characteristics, including high specific surface area, stability in most organic solvents, and abundant functional groups that can chelate with metal ions or nanoparticles to provide the necessary stability [6, 7]. Currently, metal nanoparticles stabilized by either inorganic or carbon-based materials are emerging as an efficient class of catalysts for various organic reactions [8]. Nanocatalysts are classified into two categories, heterogeneous and homogeneous. Homogeneous catalysts are known to be more active than heterogeneous catalysts due to easy contact between active sites on the catalyst and reactants in solution. However, these catalysts are difficult to isolate and recover [9-11]. Today, nanotechnology provides the possibility of designing and manufacturing heterogeneous catalysts on the nanoscale [12-14]. These catalysts have advantages such as high surface area, better particle size and shape, activity, selectivity, and can be easily separated and recycled due to their insolubility in water and most organic solvents.

Therefore, it is imperative to use renewable heterogeneous nanocatalysts for the development of green chemistry and engineering [15, 16].

In recent years, magnetic nanoparticles have emerged as promising catalysts for the synthesis of tetrazoles due to their unique properties such as high surface area, easy separation, and recyclability [17, 18].

Among theazole moieties, tetrazoles are the most nitrogen-rich stable heterocyclic ring, containing four nitrogen and one carbon atoms in a doubly unsaturated five-membered ring. They exist in various tautomeric forms, including anions and cations, such as mono- and di-substituted NH tetrazole derivatives [19-22].

Continuing our efforts to develop heterogeneous catalysts [23-27], metal-catalyzed organic transformations of magnetic biochar (MBC@BTT-Cu(II)) as a non-toxic, inexpensive biomass was synthesized and characterized. Biochar obtained from *Laurentus europaeus* plant is known as a pest of forest trees and it is necessary to remove this species. The high carbon and surface area indicate that it may be very suitable as a catalyst substrate. Their activity in the preparation of tetrazoles has been investigated.

## 2. Experimental

### 2.1. Materials

3-aminopropyltriethoxysilane, cyanuric chloride, thiourea, copper chloride hydrate, and all other reagents, chemicals, and solvents were purchased from Merck, Aldrich, Fluka and were used without additional purification.

### 2.2. The (MBC@BTT-Cu(II)) nanocatalyst synthesis

Biochar materials were prepared using slow pyrolysis of *Lauratus europaeus* plants at 700°C with a heating rate of 5°/min in N<sub>2</sub> atmosphere for 15 hours. Biochar was ground and sieved to form 20-100 mesh particles. The collected samples were stirred for 1 hour in 2 M HCl solution at room temperature to remove metal and silicate (mineral components). The biochar was thoroughly washed with deionized water. Finally, it was dried in a vacuum oven at 60°C. Synthesis of magnetic biochar (MBC): First, a homogeneous solution of FeCl<sub>3</sub>.6H<sub>2</sub>O and FeCl<sub>2</sub>.4H<sub>2</sub>O (molar ratio = 2:1) was obtained by dissolving in 100 mL of deionized (DI) water under nitrogen gas at 80°C for 10 minutes. Then 1.5 g of biochar was added in the solution and aqueous ammonia (10 mL) was added dropwise and was stirred for 1 hour. The resulting MBC was magnetically separated from the solution mixture and washed with DI water and ethanol, then dried under vacuum.

Synthesis of biochar functionalized by cyanuric chloride (MBC@NH<sub>2</sub>-CTC): 1 g of MBC was dispersed in 20 mL of toluene by sonication for 30 min and 3-aminopropyltriethoxysilane (APTES) was added to it and was stirred at 90 °C for 12 h. The resulting MBC@NH<sub>2</sub> was filtered and washed with ethanol and dried at 70°C. In the next step, MBC@NH<sub>2</sub> samples (1 g) were mixed with cyanuric chloride (2 g), then the mixture was stirred under reflux for 24 h. The solid (BC@NH<sub>2</sub>-CTC) was successively washed with water and EtOH and dried.

Synthesis (MBC@BTT-Cu(II)): Next, BC@NH<sub>2</sub>-CTC (1 g) was dispersed in 20 mL of toluene, then thiourea (1 g) and Et<sub>3</sub>N (1 cc) were added and refluxed for 24 h. MBC@BTT was filtered and thoroughly washed with ethanol. After complete drying, the obtained solid residue was used for the next step.

Preparation of MBC@BTT-Cu(II): First, 1 g of MBC@BTT was dispersed in 2 ml of alcoholic solution containing 0.05 g of copper chloride hydrate (CuCl<sub>2</sub>.H<sub>2</sub>O), the mixed solution was sonicated for 20 minutes. . The contents were stirred at room temperature for 24 h. The final MBC@BTT-Cu(II) material was separated by an external magnetic field, also washed and dried by the same methods.

### 2.3. Synthesis of 5-substituted 1H-tetrazole derivatives

The MBC@BTT-Cu(II) complex (45 mg) was added to a mixture of NaN<sub>3</sub> (1.5 mmol) and the benzonitrile derivative (1 mmol) in polyethylene glycol (PEG-400) at 120 °C it was stirred until benzonitrile was not detected by TLC. The reaction mixture was cooled, and the catalyst was magnetically separated. The reaction mixture was diluted with water and 4N HCl solution. The pure products were extracted with ethyl acetate (4x10 mL) and the residue was purified by thin layer chromatography (silica gel, hexane: ethyl acetate as eluent) to give the desired product.

## 2.4. Spectral Data

**2-(1H-Tetrazol-5-yl)-benzotrile (Table 2X, entry 1):** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>), δ (ppm): 8.19- 8.06 (m, 2H), 7.95-7.90 (t, J = 8 Hz, 1H), 7.80-7.75 (t, J = 8 Hz, 1H).

**5-(4-Chloro-phenyl)-1H-tetrazole (Table 2, entry 4):** <sup>1</sup>NMR (400 MHz, DMSO-d<sub>6</sub>), δ (ppm): 16.89 (b, 1H (N-H)), 8.07 (s, 1H), 8.05-8.02 (d, J = 8 Hz, 2H), 7.70-7.66 (d, J = 8 Hz, 2H).

**5-(2-Hydroxyphenyl)tetrazole (Table 2, entry 5):** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>), δ (ppm): 7.98 (d, J = 7.8 Hz, 1H), 7.47 – 7.34 (m, 1H), 7.12 – 6.92 (m, 2H).

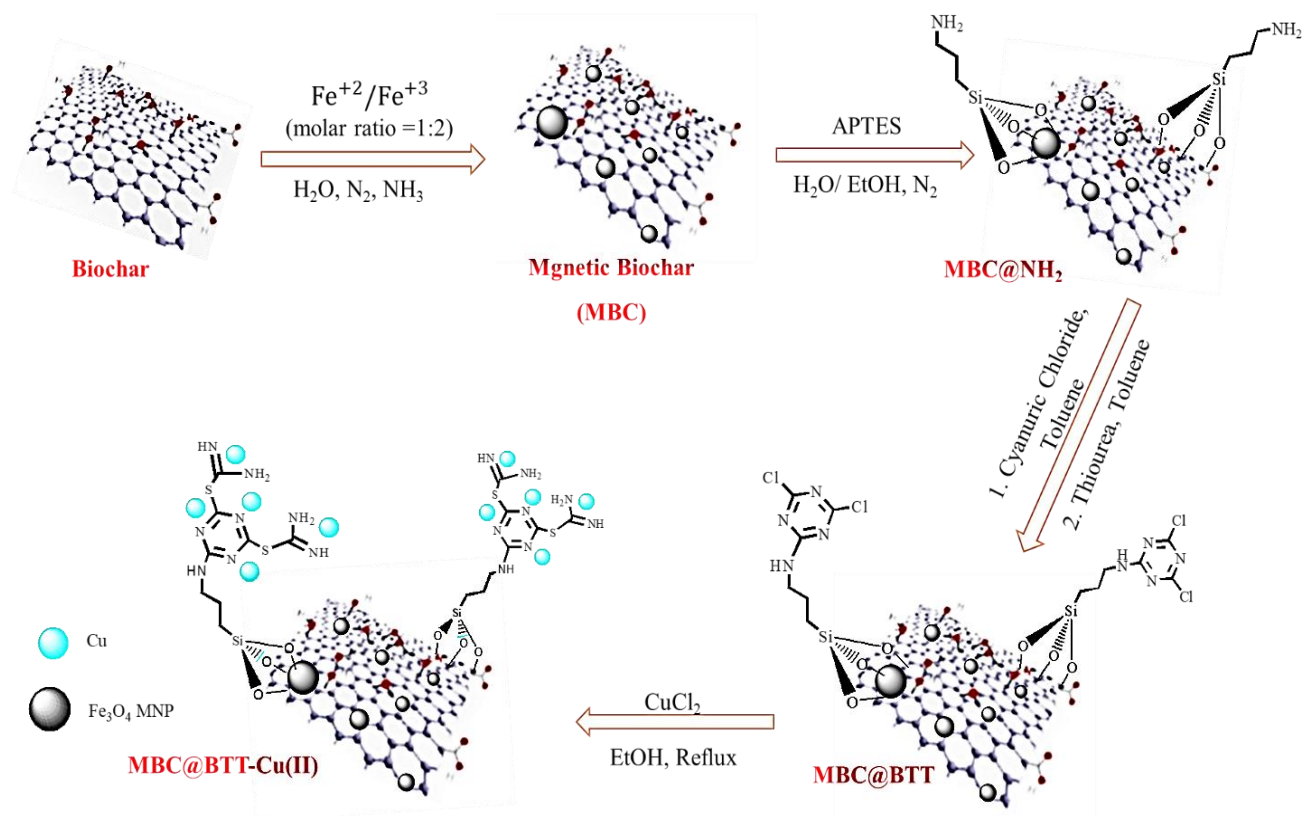
## 2.5. Characterization

SEM analysis was performed by using a FESEM-TESCAN MIRA3 scanning electron microscope. FT-IR spectra were recorded with KBr pellets using a Bruker FT-IR spectrometer (model VRTEX 70). CHNSO analysis of biochar was performed using ECS 4010 Element Analyzer from COSTECH Company. NMR spectra of products were recorded using Bruker DRX-400 spectrometer at 400 MHz. The exact content of copper was measured by AAS technique using 400pnovAA instrument from Analytik Jena Company.

## 3. Results and discussion

### 3.1. Preparation and characterization of the catalyst

In brief, biochar nanoparticles were produced by subjecting *Lauratus europaeus* plants to slow pyrolysis up to 700°C at a rate of 5°/min in an N<sub>2</sub> atmosphere for 15 hours. Fe<sub>3</sub>O<sub>4</sub> nanoparticles were used to magnetize the biochar nanoparticles, which were then modified with (3-aminopropyl)triethoxysilane. Cyanuric acid and thiourea were subsequently fixed onto the modified magnetic biochar nanoparticles, and copper intermediate metal was immobilized on their surface to create the functional nanocatalyst MBC@BTT-Cu(II) for the synthesis of 5-substituted 1H-tetrazole derivatives. The synthesis process of MBC@BTT-Cu(II) is illustrated in Scheme 1, and the catalyst was analyzed through FESEM, CHN, and AAS.

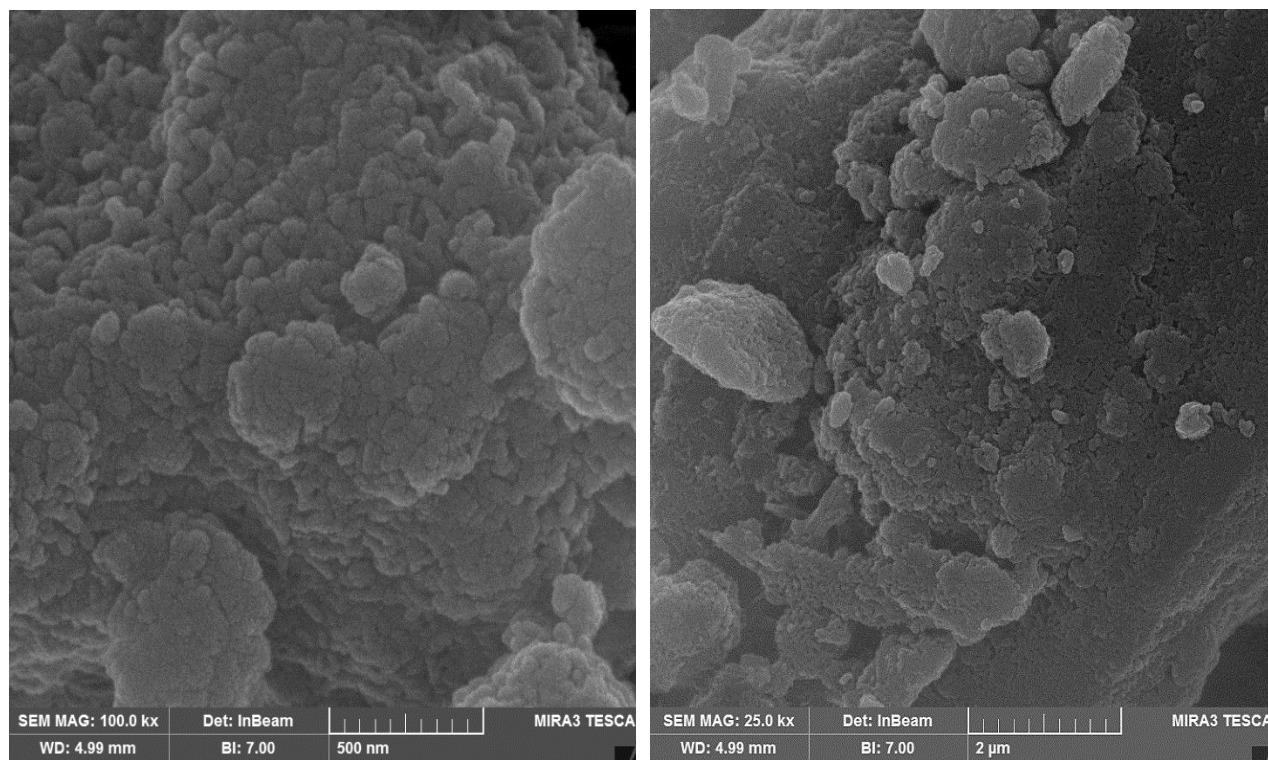


**Scheme 1.** Synthesis of MBC@BTT-Cu(II)

### 3.2. CHNS and AAS

The structure of MBC@BTT-Cu(II) nanoparticles was confirmed using SEM techniques. It can be seen from Fig. 1 that the nanoparticles have an irregular structure in the shape of a dumbbell.

The elemental composition (wt%) of biochar (BC) and MBC@BTT-Cu(II) were investigated by CHNSO analysis, biochar (BC) composed of C (72.61%), H (1.12%), O (25.26%) and N (1.01). Also, MBC@BTT-Cu(II) is composed of C (56.35 w), H (2.93 wt%), O (33.49 wt%), N (6.26 wt%), and S (0.97 wt%). As shown, the amount of S, N and H increased in MBC@BTT-Cu(II) instead of biochar (BC), indicating that the organic layer was successfully stabilized in biochar (BC). In addition, the exact amount of copper metal in the MBC@BTT-Cu(II) structure was calculated using AAS analysis, which was found to be 0.15 mmol/g [33].



**Fig. 1.** SEM images of MBC@BTT-Cu(II) with different magnifications.

### 3.3. FT-IR analysis

The FT-IR spectra of biochar (a), Fe<sub>3</sub>O<sub>4</sub> (b), MBC@BTT (c), and MBC@BTT-Cu(II) (d) are shown in Fig. 2. The OH stretching and twisting vibrations have been observed at 3000 cm<sup>-1</sup> to 3500 m<sup>-1</sup> (a–d). Fe–O stretching vibrations have been observed at 570 m<sup>-1</sup> (b–d). The C–H stretching, banding, and rocking vibrations are observed at 2855 to 2923 (a, c–d). Along with C–C and C–H bending vibrations of the compound, the vibrational bands in 1741, 1648 and 1356 m<sup>-1</sup> are attributed to C=S, C=C, groups (c). The peak appeared in 639 cm<sup>-1</sup> is indicative to synthesis of N–Cu complex in spectra d.

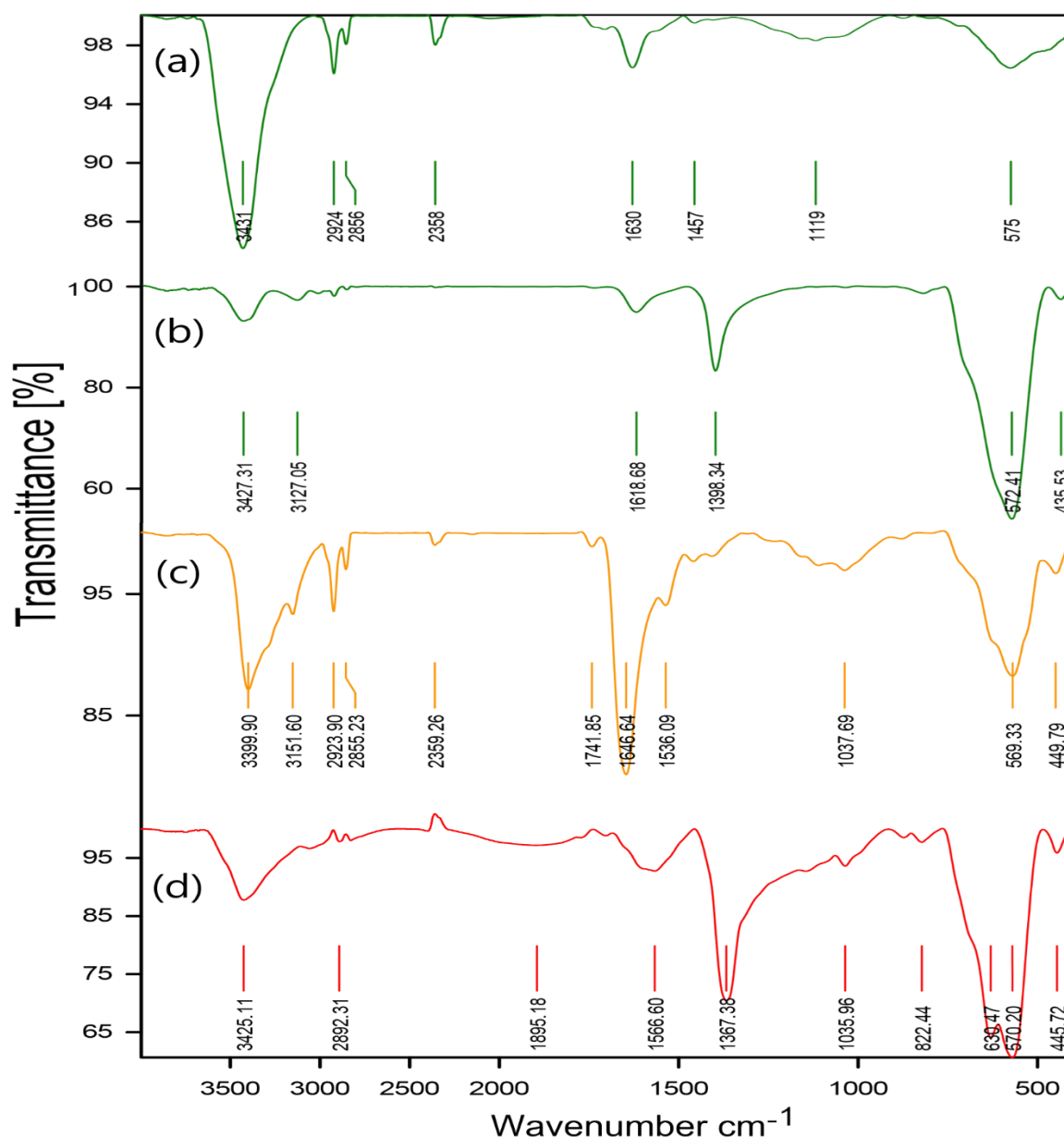


Fig. 2. FT-IR spectra for Biochar (a),  $\text{Fe}_3\text{O}_4$  (b), MBC@BTT (c), and MBC@BTT-Cu(II) (d).

### 3.4. Catalytic application of MBC@BTT-Cu(II) in the synthesis of tetrazoles

After investigating and identifying the catalyst synthesized with boehmite nanoparticles, its catalytic activity in the synthesis of tetrazole was evaluated. At first, the sodium azide reaction and benzonitrile were selected for the sample reaction and the reaction was investigated under different conditions such as solvent, catalyst amount, and temperature.

As shown in Table 1, the optimum amount of catalyst for the reaction was 45 mg, which resulted in 98% yield of the desired product. Then the effect of different chemical solvents on the reaction was investigated. It was found that conversions can be further increased by using PEG-400 as the reaction solvent. Furthermore, we observed that increasing the reaction temperature from 100 to 120°C promoted the complete conversion of benzonitrile and sodium azide via [3+2] cycloaddition. Finally, 45 mg of catalyst, PEG solvent, and 120 °C temperature was selected as optimal conditions.

**Table 1.** Screening of reaction conditions for the synthesis of tetrazoles

Entry	Catalyst	Temperature (°C)	Catalyst (mg)	Solvent	Time (min)	Yield <sup>a</sup> (%)
1	--	120	--	PEG	180	--
2	Biochar	120	45	PEG	180	N.R
3	Magnetic biochar	120	46	PEG	180	N.R
4	MBC@BTT-Cu(II)	120	15	PEG	180	45
5	MBC@BTT-Cu(II)	120	30	PEG	180	88
6	MBC@BTT-Cu(II)	120	45	PEG	25	98
7	MBC@BTT-Cu(II)	120	60	PEG	20	97
8	MBC@BTT-Cu(II)	Reflux	45	ETOH	180	N.R
9	MBC@BTT-Cu(II)	Reflux	45	DMF	180	N.R
10	MBC@BTT-Cu(II)	Reflux	45	H <sub>2</sub> O	180	N.R

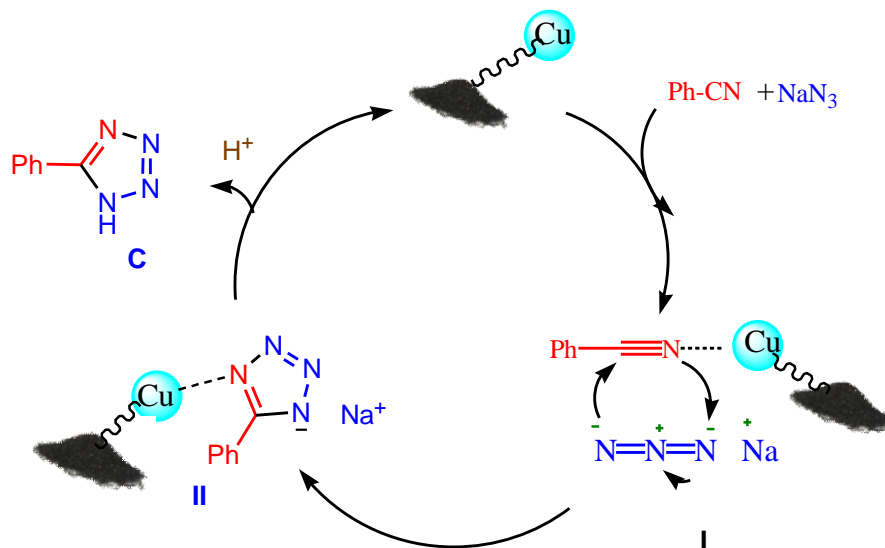
<sup>a</sup>Isolated yields.

Also, to expand the application range of MBC@BTT-Cu(II) nanocatalyst, the catalyst was used to form different tetrazole derivatives. The reaction can be performed with all substrates, including electron-donating and electron-withdrawing ones. It is worth mentioning that all those reactions gave excellent yield of tetrazole product (Table 2).

**Table 2.** The synthesis of 5-substituted 1H-tetrazoles over the catalysis of MBC@BTT-Cu(II) nanocatalyst

Entry	Nitrile	Product	Time (min)	Yield (%) <sup>a</sup>
1			25	98
2			10	94
3			15	95
4			15	98
5			20	96
6			10	97

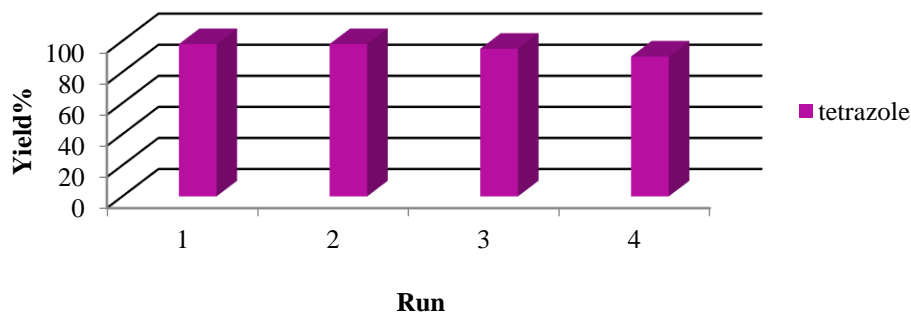
mechanism for the synthesis of tetrazoles catalyzed by Cu- MBC@BTT-Cu(II) is outlined in Scheme 2. The process starts with the approach of the nitrile to the Cu complex, leading to the intermediate R-C≡N-Cu (I). Then, the azide ion undergoes a [3+2] cycloaddition with the activated nitrile bond. The cycloaddition between the nitrile and azide takes place readily and forms an intermediate (II). Finally, the corresponding 5-aryl-1H-tetrazole product is produced via easy protonation of the anionic intermediate and acidifying the reaction using of HCl solution.



**Scheme 2.** Plausible mechanism for the click synthesis of 5-aryl-1H-tetrazoles over the catalysis of MBC@BTT-Cu(II) complex.

### 3.5. Reusability of the catalyst

To ensure economic and environmental sustainability, it is crucial for industrial applications to have catalytic systems that are both efficient and effective and can be reused multiple times. Recycling and reusing catalysts play a significant role in achieving this goal. In order to recover and reuse the MBC@BTT-Cu(II) catalyst, after the completion of a specific reaction, the catalyst was magnetically recovered and reused for 5 consecutive cycles without significant decrease in the catalyst activity (Fig. 3). These observations indicated that the catalyst was stable and tolerated the current reaction conditions.



**Fig. 3.** Recycling of catalyst for the model reaction

Considering Table 3, the results of the click synthesis of 5-aryl-1H-tetrazole in presence of the [MBC@BTT-Cu(II)] complex are compared to those of other transition metal-containing catalysts found in the literature. According to the comparative overview, the [MBC@BTT-Cu(II)] has one of the highest yields ever reported.

**Table 3.** Comparison of catalytic efficiency of [MBC@BTT-Cu(II)] complex in model reaction of synthesis of 5-aryl-1H-tetrazole

Entry	Synthesis	Catalyst	Time (min)	Yield (%) <sup>a</sup>	Reference
1	5-phenyl-1H-tetrazole	Boehmite@SiO <sub>2</sub> @Tris-Cu(I)	120	95	[28]
2	5-phenyl-1H-tetrazole	BNPs @SiO <sub>2</sub> -TPPTSA	60	96	[29]
3	5-phenyl-1H-tetrazole	Cu-Amd-RGO	30	96	[30]
4	5-phenyl-1H-tetrazole	SA-rGO	240	94	[31]
5	5-phenyl-1H-tetrazole	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @BHA-Cu(II)	70	95	[32]
6	5-phenyl-1H-tetrazole	MBC@BTT-Cu(II)	25	98	This work

#### 4. Conclusions

In summary, this study introduced MBC@BTT-Cu(II) as a non-toxic, inexpensive and recyclable catalyst for the stable synthesis of tetrazole compounds. The approach of magnetically immobilized metal-catalyzed organic transformations offers several advantages, including accessibility, non-toxicity high efficiency, use of green organic solvents, and short reaction time. MBC@BTT-Cu(II) nanocatalysts were recycled and reused five consecutive times without significant decrease in catalytic activity.

#### Conflicts of Interest

The author declares no conflict of interest.

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