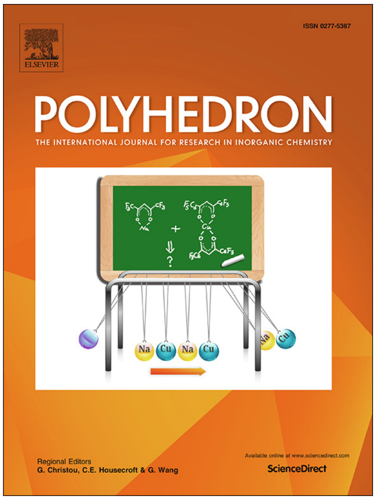

Fabricated copper catalyst on biochar nanoparticles for the synthesis of tetrazoles as antimicrobial agents

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Fabricated copper catalyst on biochar nanoparticles for the synthesis of tetrazoles as antimicrobial agents

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Abstract:

Biochar is a carbon-rich solid which its surface was covered by high density of carbonyl, hydroxyl and carboxylic acid functional groups. In this work, biochar nanoparticles were prepared from pyrolysis of chicken manure and further a new copper catalyst was supported on its surface (Cu-ABA@biochar) as reusable and environmental biocatalyst. The structure of this catalyst has been characterized by SEM, EDS, WDX, XRD, TGA, N_2 adsorption–desorption isotherms, FT-IR and AAS techniques. SEM images of this catalyst demonstrate that particle size is less than 100 nm in diameter. The catalytic activity of this nanocatalyst was studied in the synthesis of tetrazole derivatives. Tetrazole products were obtained in high TOF and TON values in the presence of Cu-ABA@biochar, which indicate the high efficiency of this catalyst. The biological activity of obtained tetrazoles was screened against several Gram-positive & Gram-negative bacteria strains which these compounds were found to possess promising activity. This catalyst was reused for several runs without significant loss of its catalytic activity or copper leaching. Also, recovered catalyst was characterized by SEM, FT-IR, AAS and N_2 adsorption–desorption isotherms. Heterogeneity and stability of this nanocatalyst was confirmed by hot filtration test and reusing of catalyst.

Key words: Biochar Nanoparticles, Copper, Tetrazoles, Biocatalyst, Antimicrobial.

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1. Introduction

Nanoparticles were emerged in various fields especially in catalysis application which they are used as catalyst directly or were used as support for heterogenization of catalysts [1-4]. Insolubility, remarkable efficiency, stability and high surface area of nanoparticles provide a suitable properties for their catalytic application [5-8]. Therefore, nanomaterials can applied as a bridge gap between heterogeneous and homogeneous catalyst [7]. In this regard, several nanomaterials were developed in the last few decades for extension of catalysis science. Among them, metal oxide nanoparticles [9], mesoporous materials [10, 11], polymers [12], graphen oxide [13], ionic liquids [14], boehmite [15, 16], MOF nanoparticles [17, 18] and carbon nanostructures [19-21] were widely used as catalyst or support. These known nanoparticles have various advantage and disadvantages meanwhile, several disadvantage are common in all of them. For example, preparation of these nanomaterials need to chemical starting materials which led to expensive procedure and also preparation of these nanomaterials is combine to generation of chemical wastes which not environmentally friendly. Therefore we introduced biochar as new support because biochar was made via pyrolysis of biological source such as agricultural wastes, green waste, woody materials, animal manures and other waste products [22-24], therefore it is inexpensive and environmentally friendly. In fact, biochar is called as black carbon which is a stable solid in air atmosphere, high temperature and aqueous solution, and was used as a soil amendment, reduction in greenhouse gas emissions from soil, agricultural waste recycling, water retention, adsorption, and climate change mitigation [23-27]. Despite, existence of several studies on biochar properties, or its application as soil amendment [27-29], biochar has been rarely used as catalyst or heterogeneous support for the immobilization of homogeneous catalysts

[22, 30, 31]. High density of carboxylic acid, carbonyl and hydroxyl groups on the surface of biochar [22, 27, 28] provide to modification of its surface for immobilization of catalysts. In this regards, we are reporting a new complex of copper on biochar nanoparticles (Cu-TBA@biochar) as efficient and reusable biocatalyst for synthesis of 5-substituted tetrazoles.

Tetrazoles are great class of five-membered and nitrogen-rich heterocyclic compounds, which have been reported as analgesic, anti-proliferative, anti-inflammatory, antibacterial, antiviral, antifungal, potential anti HIV drug candidates, herbicidal and anticancer agents [32-41]. For example olmesartan medoxomil, TAK-456, losartan and valsartan are several compounds including tetrazole core with drugs applications such as antihypertensive family drugs [33-35]. Also, tetrazoles are used in coordination chemistry as ligands and were employed as stable surrogates for carboxylic acids [38, 42]. [3 + 2] cycloaddition of azide derivatives to the nitriles is conventional method for the synthesis of 5-substituted 1H-tetrazoles [42-46].

2. Experimental

2.1. Materials and instruments

Chemicals and solvents in this work were purchased from Merck, Aldrich, or Fluka companies and used without further purification. Powder XRD of biochar nanoparticles and obtained catalyst were performed with Cu Kα radiation at 40 kV and 30 mA using a PW1730 instrument from Philips Company. Thermogravimetric analyses (TGA) of the catalyst was recorded by a SDT Q600 V20.9 Build 20 device in the temperature range of 30–800 °C under air atmosphere. The particle size and morphology of prepared nanoparticles were studied by SEM images using FESEM-TESCAN MIRA3 and FEI Quanta 200 Scanning Electron Microscopes, on an accelerating voltage of 25.0-30.0 kV. FT-IR spectra were recorded with KBr pellets using a

VRTEX 70 model Bruker FT-IR spectrometer. The component analysis was carried out by the energy dispersive X-ray spectroscopy (EDS) using an FESEM-TESCAN MIRA3 Scanning Electron Microscope. Nitrogen adsorption isotherms were obtained using a standard gas manifold at 77 K to surface characteristics of the catalyst using a BELSORP MINI II device. Also, the catalyst sample was degassed at 120 °C for 2 h using a BEL PREP VAC II device before analysis. The exact content of copper was measured by AAS technique using 400p-novAA instrument from Analytik Jena Company. 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.

2.2. Preparation of biochar

500 g of dried chicken manure was placed in a porcelain crucible. The pyrolysis temperature was selected from 400 °C to 800 °C, which is the common temperature range of pyrolysis. The set temperature reached after about 30 min of heating with the carrier gas (N_2) sweeping at 0.3 $L.min^{-1}$, and the porcelain crucibles were fed into the heating zone with an N_2 flow rate of 0.03 $L.min^{-1}$. After 1 and 2 h, the pyrolysis process was ended, and the porcelain crucibles were removed from the heating zone and cooled with N_2 sweeping at 0.3 $L.min^{-1}$ for 30 min. The solid yield was the biochar, which was ground through a 40 mesh sieve (0.45 mm). Prior to additional experiments, no pretreatment was performed. The obtained biochar was abbreviated as CMB400-1, CMB400-2 CMB600-1, CMB600-2 and CMB800-1, CMB800-2, respectively according to the pyrolysis residence time (1 and 2 h) and temperature. Carbon content, ash Content and char yield of biochar are shown in Table 1. Also, the element content of obtained biochar was studied by CHNSO analysis and the obtained results are summarized in Table 2.

Table 1. Typical char yield, ash Content and carbon content of obtained biochar

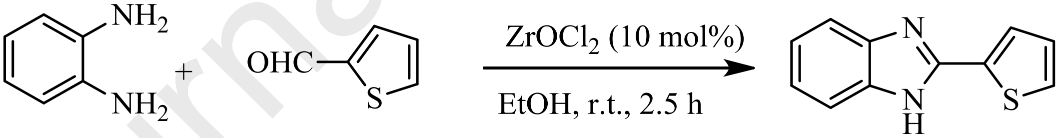
Entry	Sample	Char yield (wt.%)	Carbon content	Ash Content (%)
1	CMB 400-1	45.3	40.4	50
2	CMB 400-2	37.45	36.36	60
3	CMB 600-1	14.25	11.8	80
4	CMB 600-2	12.34	8.9	90
5	CMB 800-1	10.52	1.5	90
6	CMB 800-2	8.54	1.06	90

Table 2. Typical char yield, ash Content and carbon content of obtained biochar

Elemental analysis	C	H	N	O	S
CMB 400-1	40.4	1.8	4.2	24.24	-
CMB 400-2	36.36	1.62	3.69	21.81	-
CMB 600-1	11.8	0.42	1.15	4.72	0.14
CMB 600-2	8.9	0.32	0.68	3.5	-
CMB 800-1	1.5	0.06	0.09	0.3	-
CMB 800-2	1.06	0.15	0.02	0.21	0.15

2.3. Preparation of catalyst

Initially, 2-(thiophen-2-yl)-1H-benzo[d]imidazole (TBA) as ligand for immobilization of Copper has been synthesized according to reported procedure by Nagawade et. al. (Scheme 3) [47].



Scheme 1. Synthesis of 2-(thiophen-2-yl)-1H-benzo[d]imidazole (TBA).

Biochar nanoparticles modified by 3-choloropropyltrimthoxy silane (CPTMS@biochar) according to new reported procedure [48]; subsequently CPTMS@biochar (1.0 g) was dispersed in toluene and 1.5 mmol of TBA was added to this mixture. The mixture was stirred at 90 ºC for 48 h. The solid product (TBA@biochar) was isolated after washing with ethanol and drying at 50

˚C. The obtained TBA@biochar (0.5 g) was dispersed in 25 mL ethanol by sonication for 20 min, and then $Cu(NO_3)_2.9H_2O$ (1 mmol) was added to the reaction mixture. The reaction mixture was stirred at 80 ºC for 20 h. The final product (Cu-TBA@biochar) was filtered, washed by ethanol/water and dried at room temperature.

2.4. General procedure for the synthesis of 5-substituted 1H-tetrazoles in the presence of Cu-TBA@biochar

A mixture of NaN_3 (1.7 mmol) and benzonitrile derivative (1 mmol) in the presence of 0.050 g of Cu-TBA@biochar, were stirred at 130 °C in PEG-400; after completion of the reaction (observed by TLC), the reaction mixture was cooled down, and reaction mixture was diluted by water and ethyl acetate. Then, the catalyst was isolated by simple filtration. The remained catalyst was washed with water and ethy acete for several times. Then, aqouse solution of HCl (4 N, 10 mL) was added to the filtrated solution. The pure products extracted with ethyl acetate from water. The organic solvent was dried over anhydrous sodium sulfate, and concentrated to give the crude solid product. High purity of products was achieved using thin layer chromatography in a mixture of n-hexan and aceton as mobile phase.

2.5. Selected spectral data

5-(4-bromophenyl)-1H-tetrazole: ^1H NMR (400 MHz, DMSO): δ_H= 17.05 (b, 1H), 8.01-7.99 (d, *J*= 8 Hz, 2H), 7.86-7.84 (d, *J*= 8 Hz, 2H) ppm.

5-(4-chlorophenyl)-1H-tetrazole: ^1H NMR (400 MHz, DMSO): δ_H= 8.08-8.06 (d, *J*= 8 Hz, 2H), 7.72-7.70 (d, *J*= 8 Hz, 2H) ppm.

1-(4-(1H-tetrazol-5-yl)phenyl)ethanone: ^1H NMR (400 MHz, DMSO): δ_H= 8.22-8.19 (d, *J*= 12 Hz, 2H), 8.19-8.16 (d, *J*= 12 Hz, 2H), 2.66 (s, 3H) ppm.

4-(1H-tetrazol-5-yl)benzonitrile: ^1H NMR (400 MHz, DMSO): δ_H= 8.24-8.22 (d, *J*= 8 Hz, 2H), 8.11-8.02 (d, *J*= 8 Hz, 2H) ppm.

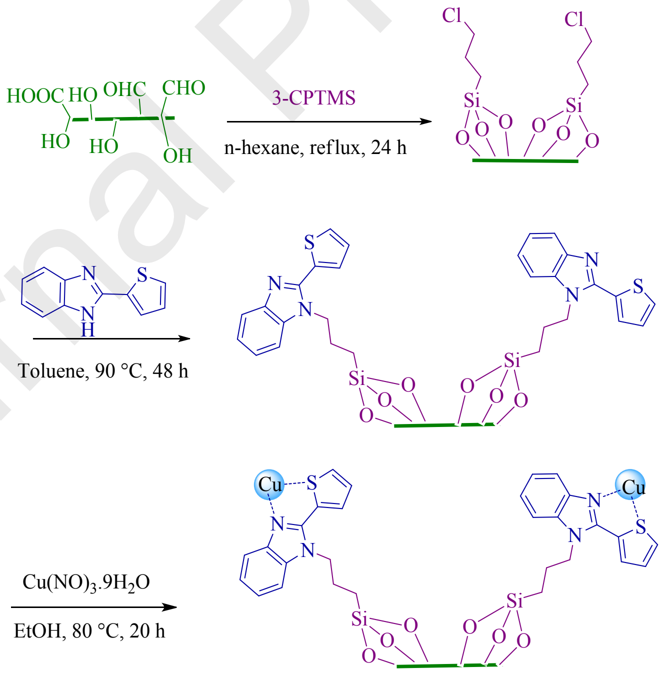
5-phenyl-1H-tetrazole: ^{1}H NMR (400 MHz, DMSO): δ_H= 8.07-8.05 (t, *J*= 8 Hz, 2H), 7.65-7.59 (m, 3H) ppm.

2-(1H-tetrazol-5-yl)benzonitrile: ^{1}H NMR (400 MHz, DMSO): δ_H= 8.15-8.09 (m, 2H), 7.99-7.94 (m, 1H), 7.84-7.81 (m, 1H) ppm.

3. Result and discussion

3.1. Catalyst preparation

In this research project, at first Cu-TBA@biochar was prepared which the procedure for the synthesis of this catalyst is outline in Scheme 1. Then Cu-TBA@biochar was characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), Brunauer-Emmett-Teller (BET), wavelength dispersive X-ray spectroscopy (WDX), and atomic absorption spectroscopy (AAS).



Scheme 1. Synthesis of Cu-TBA@biochar.

3.2. Catalyst characterizations

The SEM technique was used to studying of morphology and size of particles in free biochar and catalyst. The SEM image of free biochar was compared with SEM image of Cu-TBA@biochar. As shown in Figure 1, the particle of biochar is quasi-spherical with an average diameter about 30-70 nm which are good agreement to shape and size of Cu-TBA@biochar. These results were confirmed that particles of biochar were not any change after surface modification or immobilization of catalyst.

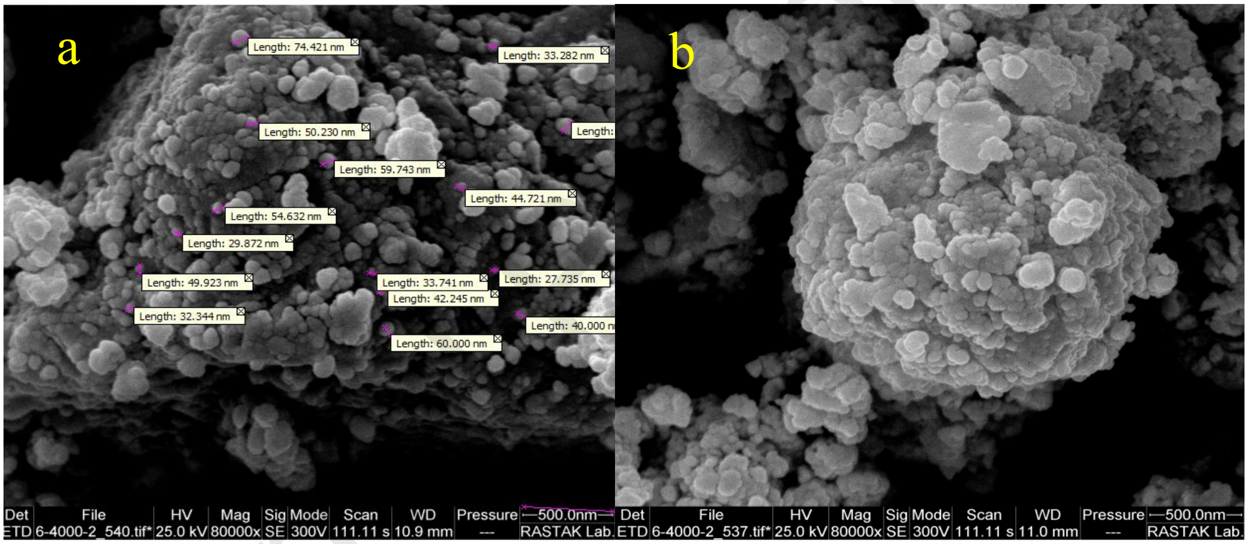


Figure 1. SEM images of (a) biochar and (b) Cu-TBA@biochar

EDS analysis was performed to determine the elements content of Cu-TBA@biochar (Figure 2) and also WDX analysis was performed to determine the elements distributions of Cu-TBA@biochar (Figure 3). As depicted, the EDS results of Cu-TBA@biochar indicate elements content of Cu-TBA@biochar as oxygen, carbon, silica, sulfur, nitrogen, and as well as copper species in the structure of the catalyst. Also, Figure 3 was shown the WDX analysis of Cu-TBA@biochar. As shown in Figure 3, the homogeneous distribution of oxygen, carbon, silica, sulfur, nitrogen, and copper was clearly observed in WDX analysis from Cu-TBA@biochar.

Also, the exact amount of copper in the structure of Cu-TBA@biochar was evaluated by AAS analysis that found to be 0.78 × 10^{-3} mol g^{-1}.

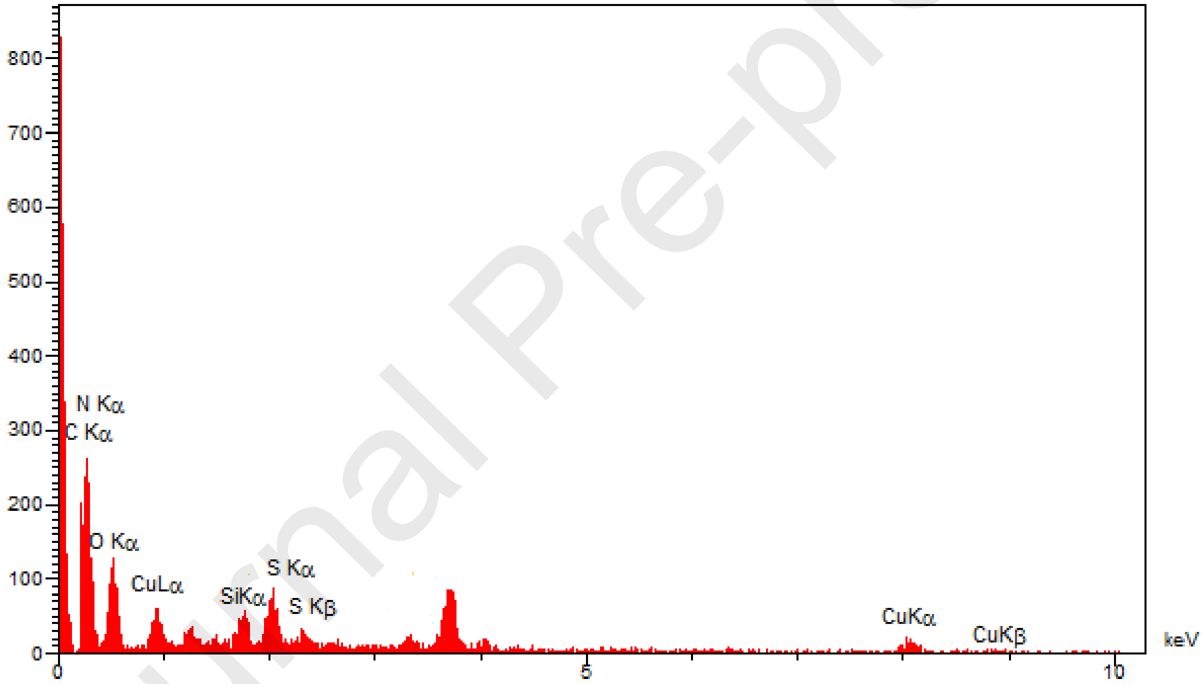


Figure 2. EDS diagram of Cu-TBA@biochar.

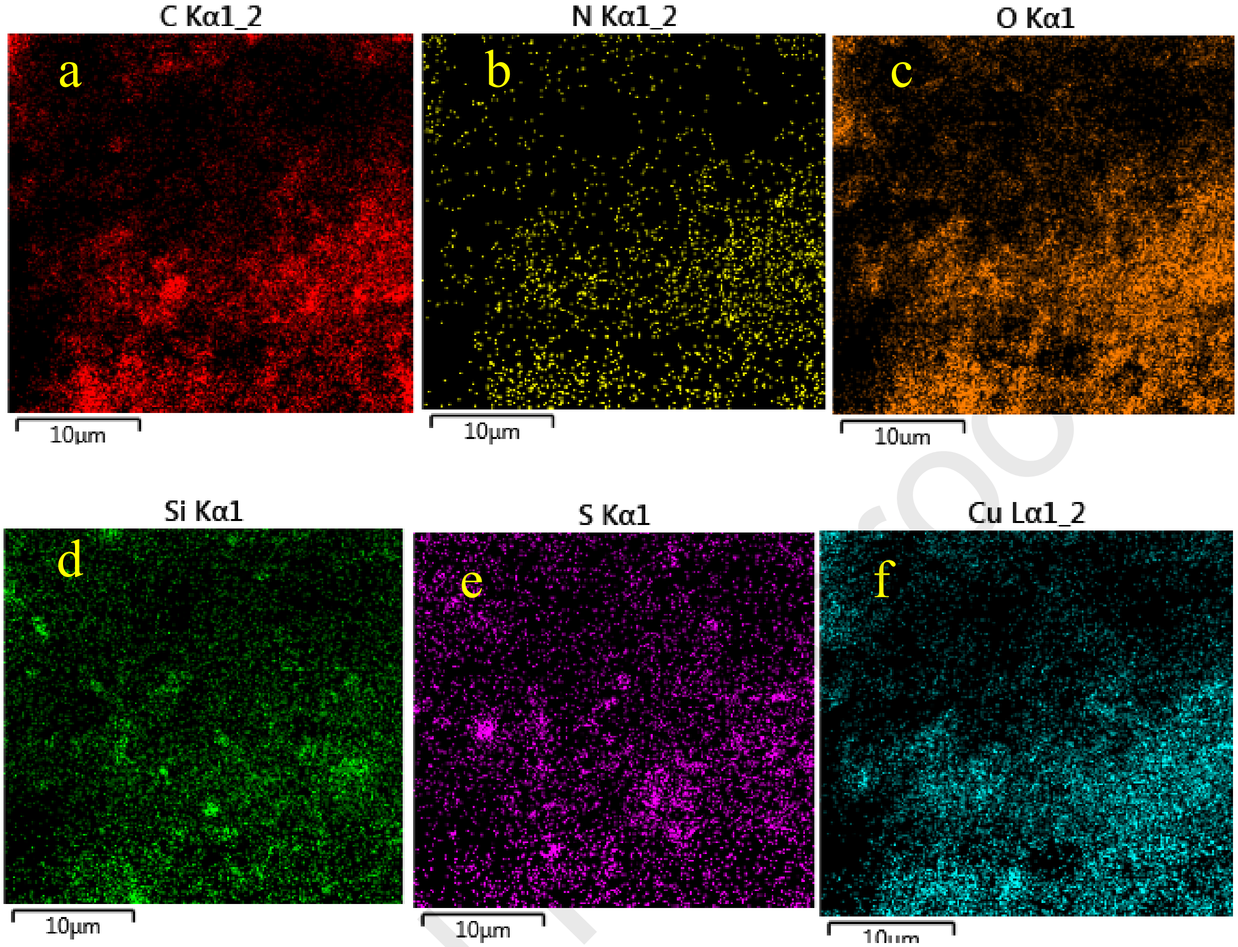


Figure 3. Elemental mapping of (a) carbon, (b) nitrogen, (c) oxygen, (d) silica, (e) sulfur, and (f) copper for Cu-TBA@biochar.

TGA diagram of Cu-TBA@biochar is shown in Figure 4. This diagram shows a small mass loss about 4% in the low temperature which is lower than 150 °C. This weight loss related to the evaporation and removal of adsorbed solvents [38]. The TGA diagram of the Cu-TBA@biochar was shown a mass loss between 300-600 °C which is about 50 %. This mass loss can be related to the organic content in catalyst [14]. As shown in Figure 4, no weight loss was not observed between 150-300 °C which is indicate the stability of catalyst up to 300 °C. Therefore this catalyst can be applied for organic reaction in high temperatures and hard conditions. Based on these results, an interesting advantage of Cu-TBA@biochar as catalyst is high thermal stability which allowed that application of this catalyst can be extended for wide ranges of organic reactions.

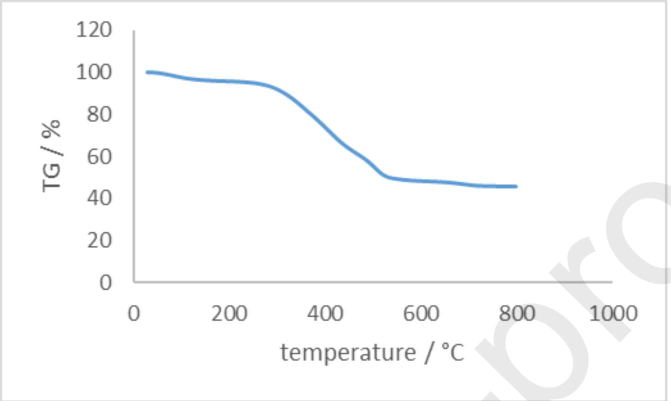


Figure 4. TGA diagram of Cu-TBA@biochar.

The normal XRD patterns of free biochar and Cu-TBA@biochar are shown in Figure 5. A sharp peaks at 2θ°=30° were shown in the XRD patterns of biochar and Cu-TBA@biochar which is agreement to standard XRD pattern of biochar [31, 49]. Figure 5 also shows several weak peaks at 2θ°=40.7°, 43.7°, 48.7° and 66.7° for XRD patterns of biochar and catalyst [49]. As shown in Figure 5, XRD pattern of biochar shows a good agreement with XRD pattern after modification.

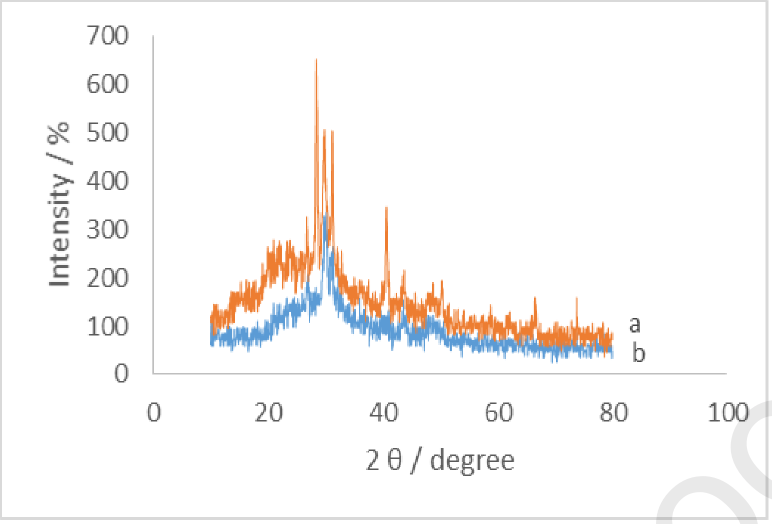
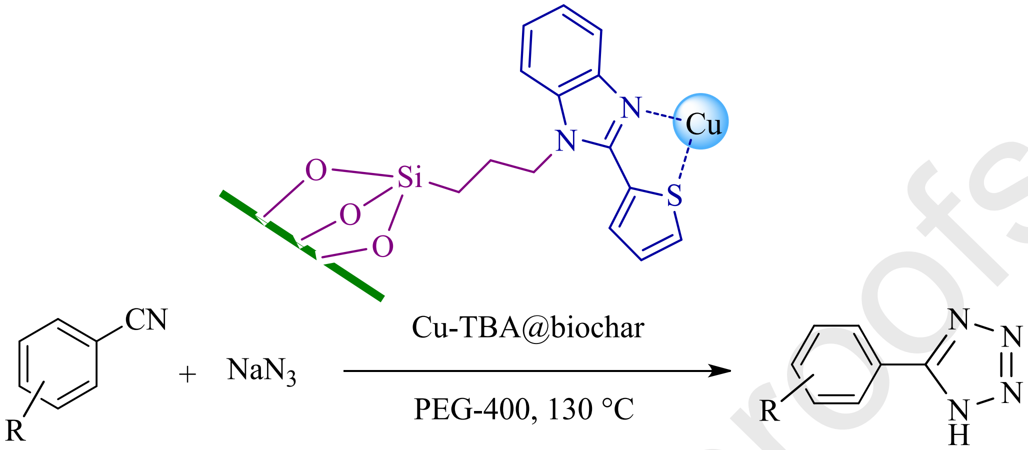


Figure 5. Normal XRD pattern of biochar (a) and Cu-TBA@biochar (b).

3.3. Catalytic application of Cu-TBA@biochar in the synthesis of tetrazoles

The catalytic activity of Cu-TBA@biochar was studied in the synthesis of tetrazole derivatives. Synthesis of tetrazole derivatives is shown in Scheme 2. In the first step, [3 + 2] cycloaddition of sodium azide and benzonitrile was selected as model reaction to optimization of reaction conditions. This model reaction was examined in various parameters such as different amount of catalyst, several solvent and wide range of temperatures. The obtained results from these experiments are summarized in Table 3. As shown in Table 3 (Entry 5), the best results (including product yield and reaction time) were obtained in the presence of 50 mg (containing 0.78 mol%) of Cu-TBA@biochar. Decreasing in the amount of catalyst from 50 to 40 mg was led to decreasing in yield of product and increasing in reaction time (Table 3, entry 2). Also, among the various solvents, the best results were obtained in PEG-400. When PEG-400 was used as solvent, 98% of products were obtained after 7 h. while, when H_2O, DMSO, DMF and ethanol were used as solvent, 59%, 43%, 30% and 38% of products were obtained respectively after 7 h.

Therefore, PEG-400 was selected as solvent. Finally, the wide ranges of temperatures (between room temperature-130 °C) were also studied and the best results were obtained at 130 °C.



Scheme 2. Synthesis of tetrazoles in the presence of Cu-TBA@biochar

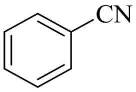
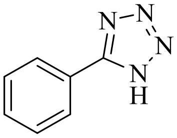
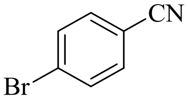
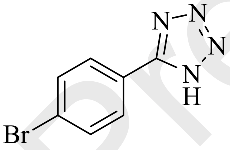
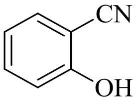
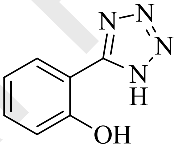
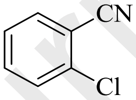
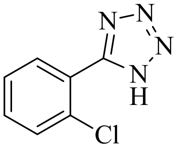
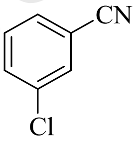
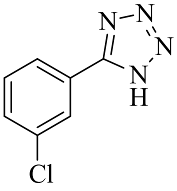
Table 3. Optimization reaction conditions for the synthesis of tetrazoles in the presence of Cu-TBA@biochar.

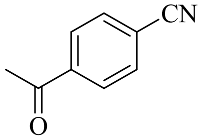
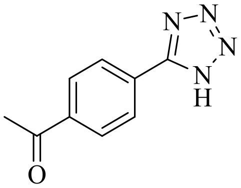
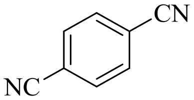
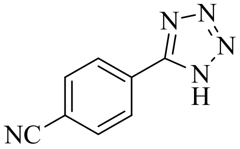
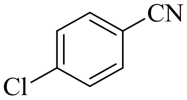
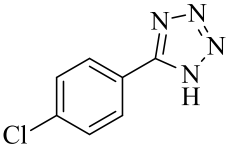
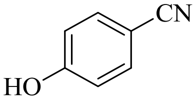
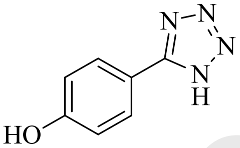
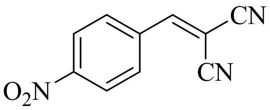
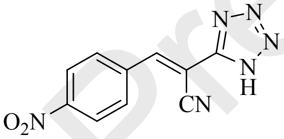
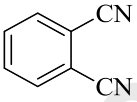
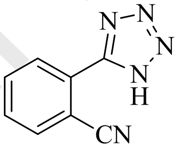
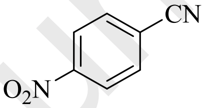
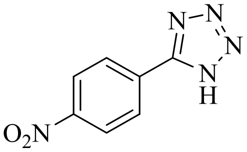
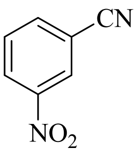
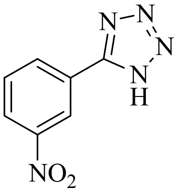
Entry	Catalyst (mg)	Solvent	Temperature (ºC)	Time (h)	Yield (%)[a]
1	-	PEG	120	24	N.R
2	40	PEG	120	22	84
3	50	PEG	120	20	95
4	60	PEG	120	17	93
5	50	PEG	130	7	98
6	50	DMSO	130	7	43
7	50	DMF	130	7	30
8	50	H_2O	Reflux	7	59
9	50	EtOH	Reflux	7	38
10	50	PEG	r.t	7	N.R

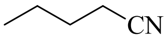
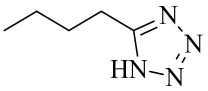
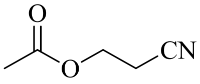
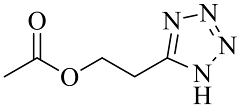
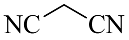
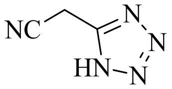
[a] Isolated yield.

The catalytic activity of Cu-TBA@biochar was explored in [3 + 2] cycloaddition of sodium azide with various benzonitrile derivatives (Table 4). Aliphatic and aromatic nitriles bearing electron-donating or electron-withdrawing groups were studied and corresponding tetrazoles were obtained in high yields and high TOF values. High TON and TOF values were indicate the high efficiency of Cu-TBA@biochar in the synthesis of tetrazole derivatives. Interestingly, dicyano substituted derivatives such as phthalonitrile (Table 4, entry 11), terephthalonitrile (Table 4, entry 7), malononitrile (Table 4, entry 16) and 2-benzylidenemalononitrile derivatives (Table 4, entry 10) were afforded the mono addition products. Therefore this procedure can be explored for wide ranges of nitriles.

Table 4 Synthesis of tetrazole derivatives in the presence of Cu-TBA@biochar.

Entry	Nitrile	Product	Time (min)	Yield (%)[a]	TON	TOF (h^{-1})
1			420	98	125.6	18.4
2			680	95	121.8	10.7
3			15	96	123.1	492.4
4			75	96	123.1	98.5
5			405	98	125.6	18.6

6			530	92	117.9	13.3
7			140	97	124.3	53.3
8			140	89	114.1	48.9
9			75	91	116.7	93.4
10			95	93	119.2	75.3
11			70	91	116.7	100
12			300	88	112.8	22.6
13			270	95	121.8	27.1

14			53	90	115.4	130.6
15			120	85	109	54.5
16			25	96	123.1	295.4

[a] Isolated yield after purification.

3.4. Antimicrobial activity tetrazoles

The antibacterial activity of 5-(3-nitrophenyl)-1H-tetrazole (Table 4, entry 13) and 4-(1H-tetrazol-5-yl)phenol (Table 4, entry 9) was evaluated by determination of their minimum inhibitory concentrations (MICs) by using agar dilution method. For this regard, growth medium of Mueller-Hinton agar was used for antibiotic susceptibility testing. The inhibitory effects of this compounds was studied against bacterial strains which comprise of three Gram negative bacteria and three Gram positive bacteria. Escherichia coli (ATCC 25922), Klebsiella pneumoniae (ATCC 25926) and Pseudomonas aeroginosa (ATCC 27853) were selected as Gram negative bacteria, also Bacillus cereus (ATCC 6177), Staphylococcus aureuse (ATCC 25923) and Streptococcus agalactiae (ATCC 12232) were selected as Gram positive bacteria. The MIC values are compared with standard drugs Tetracycline (30 mg/mL) and Gentamicin (10 mg/mL). At a glimpse, 5-(3-nitrophenyl)-1H-tetrazole (**13a**) has no antibacterial effect. Meanwhile, 4-(1H-tetrazol-5-yl)phenol (**9a**) showed significant antibacterial activity against of both Gram negative and Gram positive bacteria. Compound **9a** showed a good inhibitory efficiency against of Escherichia coli (MIC 10 mg/mL), Klebsiella pneumoniae (MIC 5 mg/mL) and

Staphylococcus aureuse (MIC 10 mg/mL). 5 mg/mL of **9a** has a lower inhibitory effect against Klebsiella pneumoniae than 10 mg/mL of it.

3.5. Recyclability of the catalyst

The recovering and recycling of the Cu-TBA@biochar were studied in the synthesis of 5-(2-chlorophenyl)-1H-tetrazole using [3 + 2] cycloaddition of sodium azide with 2-chlorobenzonitrile as model reaction. In this regard, after completion of each reaction, reaction mixture was diluted by ethyl acetate and water. Then, the catalyst was recovered by centrifugation. The remained catalyst was washed with ethy acete and water for several times. Then, aqouse solution of HCl (4 N, 10 mL) was added to the filtrated solution. 5-(2-chlorophenyl)-1H-tetrazole as product extracted with ethyl acetate from water. The recovered catalyst was reused in the next run. The obtained results from recycling of Cu-TBA@biochar are summarized in Figure 6. As shown in Figure 6, this catalyst can be recycled up to 8 times without significant loss in its catalytic activity.

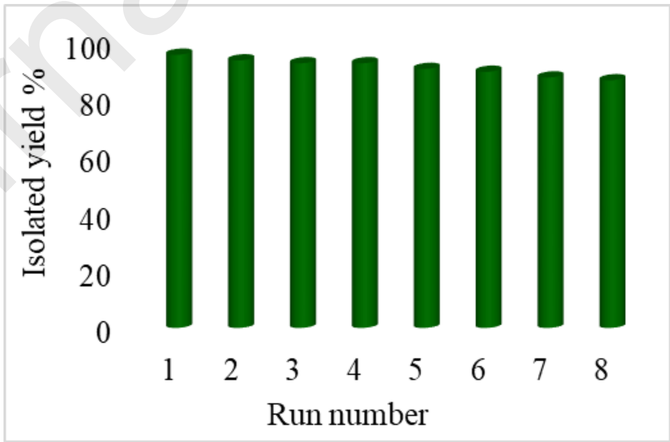


Figure 6. Recyclability of Cu-TBA@biochar in synthesis of 5-(2-chlorophenyl)-1H-tetrazole.

3.6. Leaching Study of catalyst

In order to studying of metal leaching in the reaction mixture, hot filtration test was performed. For this regard, [3 + 2] cycloaddition of sodium azide with benzonitrile was selected and further in half-time of the reaction (the half-time of this reaction is 210 minutes), the product was isolated which 47% of product was obtained. Then, this reaction was repeated, meanwhile after half-time of reaction, catalyst was remover and then permitted to continue reaction for the filtrated solution. In this stage, after 7 h the product was obtained in 52% of yield. These experiments confirm that leaching of copper did not occur.

In order to explore the studding about of heterogeneous nature of Cu-TBA@biochar, copper concentration in reaction solution was calculated by AAS analysis. In this regard, reaction of sodium azide and benzonitrile was repeated under optimized conditions. Then, catalyst was removed by filtration after 210 min and further the filtered solution was analyzed by AAS technique. In this analysis, the copper concentration in solution was very small, which found to be 6.7×10^{-6} mmol mL^{-1}. This very small amount of cooper did not have a significant effect on the reaction progress. Therefore completion of the reaction could be attributed to the supported copper on biochar.

3.7. Characterization of recycled catalyst

In order to indicate the stability of Cu-TBA@biochar after recovering and reusing, recovered catalyst was characterized by SEM, BET, AAS and FT-IR techniques. The morphology and particle size of Cu-TBA@biochar after recycling has been studied by SEM technique. The SEM image of reused Cu-TBA@biochar is shown in Figure 7. As shown in this Figure, the size and morphology of catalyst after reusing is shown a good agreement to fresh catalyst, which is about

30–70 nm in diameters . also, the shape of recycled catalyst was shown a good similarly to fresh catalyst. In addition, AAS analysis of reaction solotion confirmed that copper leaching was not happend under reaction conditions, which proves that Cu-TBA@biochar has heterogeneous nature.

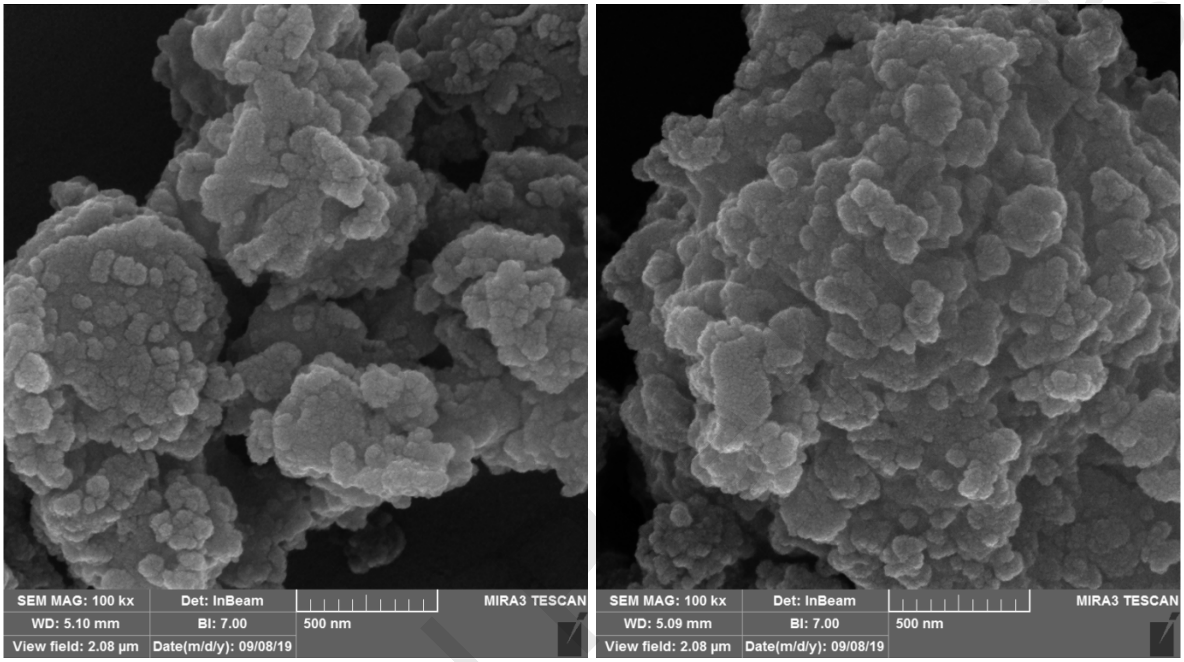


Figure 7. SEM images of recovered Cu-TBA@biochar

Nitrogen adsorption–desorption isotherms of recoverd and fresh catalyst are shown in Figure 8. Also, textural properties of biochar, catalyst and recovered catalyst are summarized in Table 5. Based on Brunauer-Emmett-Teller (BET), the BET surface area [31], pore volumes [31] and pore diameters [31] of biochar are higher than fresh and recoverd catalyst which is due to the grafting of organic layers and Cu-complex on the surface of biochar nanoparticles. Meanwhile, a good agreement was observed between textural properties of recoverd and fresh catalyst.

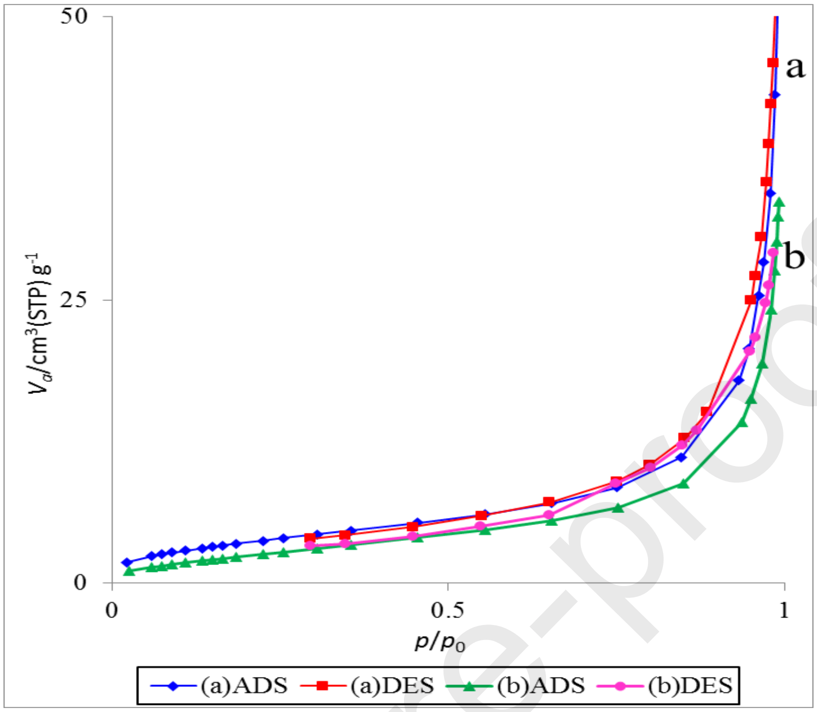


Figure 8. Typical N_2 adsorption–desorption isotherm of fresh (a) and recovered (b) Cu-TBA@biochar

Table 5. Textural properties of biochar, fresh and recovered Cu-TBA@biochar.

Entry	Sample	S_{BET} (m^2/g)	Pore diameter (nm)	Pore volume (cm^{3}g^{-1})
1	Biochar	199-557 [31]	2.4-3.0 [31]	0.03-0.22 [31]
2	Fresh Cu-TBA@biochar	16.4	1.29	0.08
3	Recovered Cu-TBA@biochar	14.4	1.29	0.05

FT-IR spectra of recovered catalyst was compared to FT-IR spectra of fresh catalyst which are shown in Figure 9. As shown in Figure 9, good agreement was observed for FT-IR spectra of fresh and recovered catalyst. Stability of Cu-TBA@biochar after recycling was confirmed with position of stretching vibrations in FT-IR spectra of fresh and recycled catalyst which are sammurized in Table 6. These results are strong evidence for stability of Cu-TBA@biochar in reaction conditions.

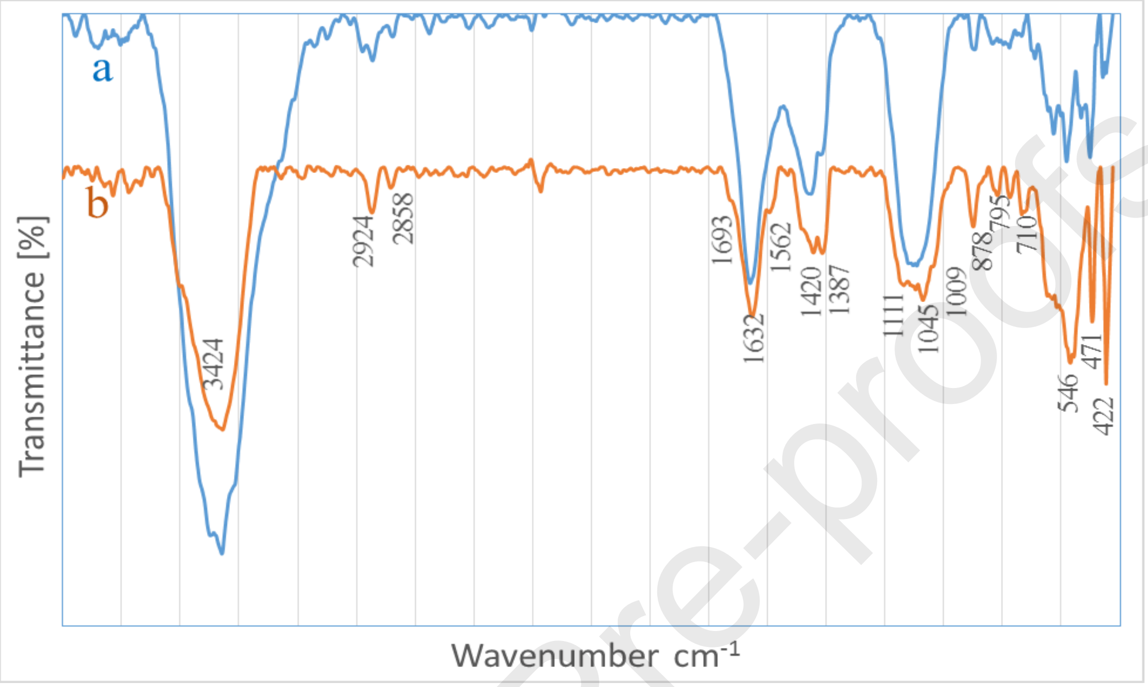


Figure 9. FT-IR spectra of fresh (a) and recovered (b) Cu-TBA@biochar

Table 6. FT-IR characteristic absorption of fresh and recovered Cu-TBA@biochar.

Entry	Functional group	Absorption (cm^{-1})	Reference
1	C–H stretch	2858-2924	[5, 50]
2	C–H bending	878	[30]
3	C=C bending	1562	[30, 31]
4	O–H stretch	3200-3650	[16, 50]
5	O–H bending	1387	[30, 31]
6	C=N stretch	1632	[7, 51]
7	C=O stretch	1693	[22, 31]
8	Si-O	471, 795, 1075	[52]
9	C-O and C-N stretch	1009-1111	[30, 31]
10	C-S stretch	710-795	[53]

3.8. Comparison of the catalyst

In order to shown the efficiency of Cu-TBA@biochar, this catalyst was compared with previous methods in the [2+3] cycloaddition reaction of benzonitrile with sodium azide (Table 7). As shown in Table 7, the TON and TOF values and also obtained yield in the presence of Cu-TBA@biochar are higher than previous catalysts. Also biochar is inexpensive and environmentally friendly in comparison with other supports because biochar is made *via* pyrolysis of biological source such as agricultural wastes and green wastes. Also, many previously reported methods were used of homogeneous catalysts which cannot recovered and reused. While, Cu-TBA@biochar was recycled for several runs in synthesis of 5-(2-chlorophenyl)-1H-tetrazole without significant loss of its catalytic activity, which demonstrates the practical reusability and efficiency of this catalyst.

Table 3. Comparison of Cu-TBA@biochar in the synthesis of 5-phenyl-1H-tetrazole with previously reported procedures.

Entry	Catalyst	Condition	Time (h)	Yield (%)	TOF (h^{-1})	Ref.
1	$(NH_4)Ce(NO_3)_6$	DMF, 110ºC	6	97	1.61	[35]
2	Sm@l-MSN	DMF, 100 ºC	5	87	40.7	[42]
3	Fe_3O_4@SiO_2/Salen Cu(II)	DMF, 120ºC	7	90	-	[54]
4	ammonium chloride and ammonium fluoride	DPOL/H_2O (6/4), 160ºC	48	95	0.10	[55]
5	$AgNO_3$	DMF, 120ºC	5	83	1.66	[56]
6	$Cu(OAc)_2$	DMF, 120ºC	12	98	0.32	[57]
7	CAN supported HY-zeolite	DMF, 110ºC	4	93	0.77	[40]
8	$FeCl_3$–SiO_2	DMF, 120ºC	12	79	-	[58]
9	Fe_3O_4@SiO_2/aza-crown ether-Cu(II)	PEG-200, 100 ºC	2.5	95	38	[59]
10	Cu-TBA@biochar	PEG, 130ºC	7	98	18.4	This work

4. Conclusion

In conclusion, biochar was prepared from chicken manure and was used as support for immobilization of copper as catalyst. At first this catalyst was characterized by SEM, EDS, WDX, AAS, FT-IR, N_2 adsorption–desorption isotherms, TGA and XRD techniques and further the catalytic activity of this catalyst was studied in the synthesis of tetrazoles. All products were obtained in good turnover numbers (TON), turnover frequency (TOF) and yields. The biological activity of obtained tetrazoles was screened against several Gram-positive & Gram-negative strains which these compounds showed significant antibacterial activity against of both Gram negative and Gram positive bacteria. Also this catalyst can be recovered and recycled for several times without any significant loss of its activity and stability of catalyst after recycling was confirmed by SEM, FT-IR, AAS and N_2 adsorption–desorption isotherms. Heterogeneity nature of Cu-TBA@biochar as catalyst was studied by recycling of this catalyst and hot filtration test.

Acknowledgment

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Graphical Abstract

Fabricated copper catalyst on biochar nanoparticles for the synthesis of tetrazoles as antimicrobial agents

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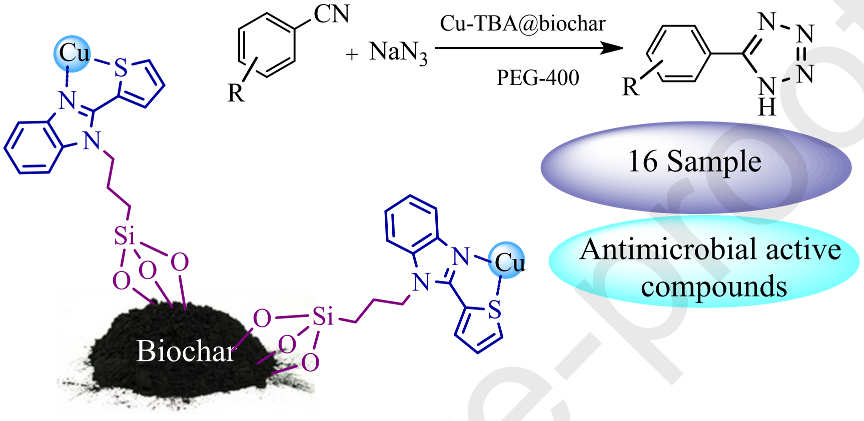

Cu-TBA@biochar

In this work, biochar nanoparticles were prepared from pyrolysis of chicken manure and further a new copper catalyst was supported on its surface (Cu-ABA@biochar) for the synthesis of antimicrobial derivatives of tetrazole in high TOF and TON values. The biological activity of obtained tetrazoles was screened against several Gram-positive & Gram-negative bacteria strains. The structure of this catalyst has been characterized by SEM, EDS, WDX, XRD, TGA, N_2 adsorption–desorption isotherms, FT-IR and AAS techniques.