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Chitosan supported 1-phenyl-1*H*-tetrazole-5-thiol ionic liquid copper(II) complex as an efficient catalyst for the synthesis of arylaminotetrazoles

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ABSTRACT

A recyclable functional hybrid catalyst was prepared *via* a simple method using chitosan as a linear polysaccharide and an ionic liquid. In this work, the synthesis of chitosan supported 1-phenyl-1*H*-tetrazole-5-thiol ionic liquid copper(II) complex (CS@Tet-IL-Cu(II)) was investigated. The synthesized CS@Tet-IL-Cu(II) was characterized using XRD, EDS, elemental mapping, STEM, FT-IR, TG/DTA, ICP-MS and TEM analyses. CS@Tet-IL-Cu(II) was applied as an effective and novel catalyst in the synthesis of arylaminotetrazoles *via* the cycloaddition reaction of arylcyanamides and NaN_3 in DMF solvent. The experimental results indicated that the type of substituents on arylcyanamides could affect the type of products (A or B isomer). The arylcyanamides with electron withdrawing and donating groups can produce isomer A (5-arylamino-1*H*-tetrazole) and isomer B (1-aryl-5-amino-1*H*-tetrazole), respectively. In addition, CS@Tet-IL-Cu(II) can be reused five times with no noteworthy loss of performance.

1. Introduction

In recent years, tetrazole compounds have made many contributions to chemistry, medicine, and pharmaceuticals. Tetrazoles can be applied as isosteres of carboxylic acids, ligands in a variety of complexes, as well as explosives in different propellants [1–5]. Tetrazole anions are ten times more lipophilic than carboxylate anions, which is an important feature in the design of different drug molecules to penetrate cell membranes [6–8]. In addition, tetrazoles are applied as herbicides, plant growth regulators, and fungicide stabilizers in agriculture [9–11]. Tetrazole is a 5-membered ring with special properties including high acidity and enthalpy of formation as well as high N number. In addition, tetrazoles are very stable [12–14]. Various tetrazole derivatives have been successfully used as efficient compounds in the preparation of *N*-containing compounds [15,16]. Tetrazole containing compounds have various applications; especially in medicine, such as antihypertensive drugs and antitumor agents [17,18].

There are some methods for the preparation of arylaminotetrazoles. Due to the many benefits and applications of arylaminotetrazoles, there are several methods to synthesize them (Scheme 1) [19,20]. Some of the methods shown in Scheme 1 for the synthesis of aminotetrazoles have drawbacks including the use of non-safe azide sources, expensive reagents, and homogeneous catalysts, harsh reaction conditions as well as tedious workup, low yield, and production of a mixture of different isomers [21].

Recently, arylaminotetrazoles have been synthesized by the [2 + 3] cycloaddition reaction of monosubstituted cyanamides and sodium azide (NaN_3). Due to some advantages of heterogeneous catalysts, researchers have used them in the synthesis of arylaminotetrazoles [22–26].

Heterogeneous catalysts are one of the most promising compounds for different reactions. One of the most significant steps in the fabrication of heterogeneous catalysts is to select a suitable support for the decoration of metal nanoparticles or complexes [27–34]. Natural polymers or biopolymers, for example cellulose, alginate, starch, gum, chitin, and chitosan are the most promising compounds, which are broadly applied as efficient supports in the synthesis of heterogeneous catalysts. In recent years, among the various biopolymers, chitosan has attracted a lot of attention due to its many benefits. In fact, chitosan is a hydrophobic and linear polysaccharide, which is prepared by deacetylation of chitin in an alkaline solution. Chitin, which is the most abundant polysaccharide after cellulose, is obtained from the exoskeletons of shrimp, crabs, and squid (Fig. 1). In addition, chitosan is a cationic polysaccharide with some advantages including biodegradability, accessibility, biocompatibility, and none-toxicity. These advantages make chitosan a suitable and biodegradable choice for the preparation of heterogeneous catalysts [21].

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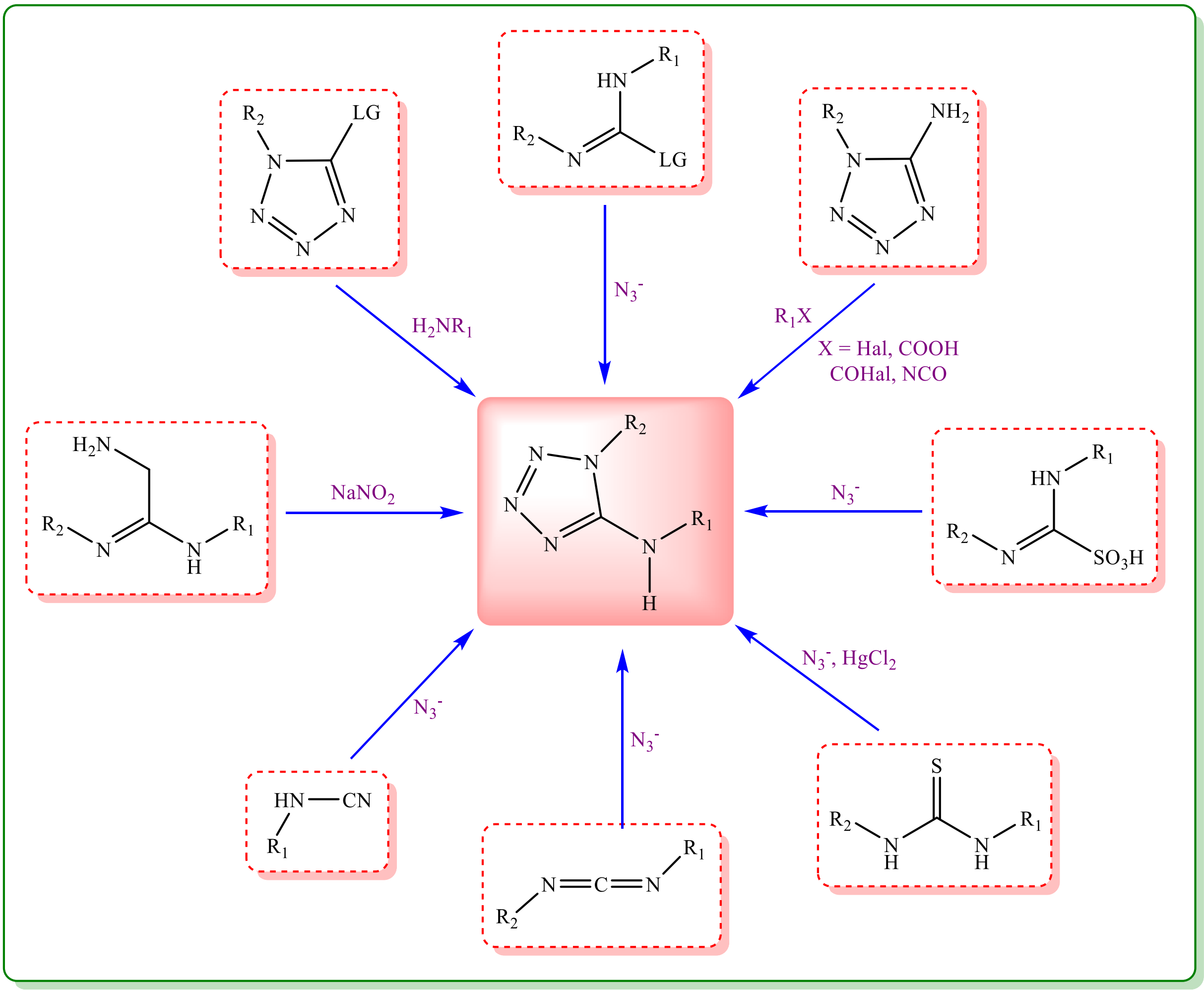


Scheme 1. Different methods for the synthesis of aminotetrazoles.

Ionic liquids (ILs), which are a novel class of eco-friendly, safe solvents composed mainly of ions, are applied in various applications; especially in catalysis. In other words, ILs can play different roles as catalysts, reagents, reaction media, and solvents. Nowadays, the use of ILs as catalysts is very much considered by researchers because they have many benefits such as high thermal stability, recyclability, and exceptional solvation properties [35,36].

An efficient heterogeneous metal ionic liquid catalyst (CS@Tet-IL-Cu(II)) by 1-phenyl-1*H*-tetrazole-5-thiol has been designed and characterized in this work. In other words, 1-phenyl-1*H*-tetrazole-5-thiol ionic liquid Cu(II) complex has been supported on chitosan using (3-chloropropyl)trimethoxysilane. To the best of our knowledge, this is the first report on the synthesis of a tetrazole based ionic liquid stabilized on the surface of chitosan. Although there are several reports concerning imidazole based ionic liquids [28], very few ionic liquid based tetrazoles have been synthesized [29,37,38]. However, it is noteworthy that there are no reports on the synthesis of ionic liquids using 1-phenyl-1*H*-tetrazole-5-thiol. Therefore, this report could create a new route for the synthesis of ionic liquid based tetrazoles. Next, the prepared CS@Tet-IL-Cu(II) was applied in the preparation of arylaminotetrazole derivatives by [2 + 3] cycloaddition reaction of a wide range of substituted arylcyanamides and NaN_3 in DMF solvent (Scheme 2). The results show that the CS@Tet-IL-Cu(II) has excellent catalytic activity and the products are obtained in good yields. The use of a relatively inexpensive catalyst, generality, efficiency, short reaction time, simplicity, easy work-up procedure, reusability of the catalyst, straightforward isolation of the products, and the high yield of products are the advantages of this protocol.

2. Experimental

2.1. Tools and chemicals

All chemicals were obtained from Merck and Aldrich Chemical Co. Chitosan (De-acetylation degree: 85%, molecular weight: 50,000–80,000 Da (medium), particle dimension: powder with a mesh size of 80, soluble in 1% acetic acid) was supplied by Nano Novin Polymer (NNP) Co. Company. The structure of the synthesized heterogeneous catalyst was characterized using FT-IR, XRD, TEM, FESEM, and EDS analyses. The products were characterized by FT-IR, ^{1}HNMR, and ^{13}CNMR. The FT-IR and NMR spectra were recorded using Perkin-Elmer 781 and Bruker spectrophotometer and Avance DRX-400 and 600 MHz, respectively. The morphology and size of the prepared catalyst were obtained by TEM using JEM-F200 JEOL, and FESEM, Hitachi S-4700 instruments. The XRD and TG/DTA analyses were performed using Philips PW 1373 diffractometer and STA 1500 Rheometric-Scientific, respectively. The elemental contents of the catalyst were determined by inductively coupled plasma optical emission spectrometry (ICP-MS, Perkin Elmer, Optima 8000).

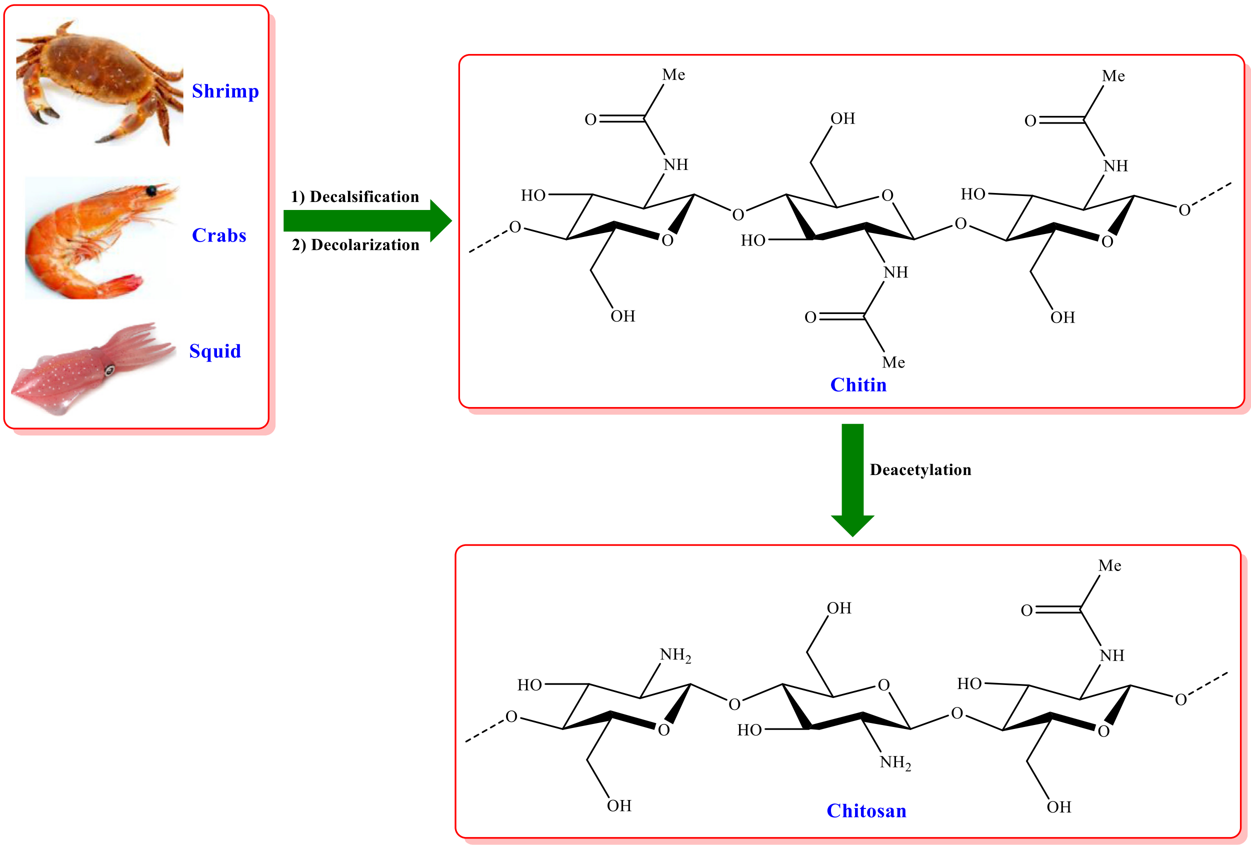


Fig. 1. Schematic representation of the preparation of chitosan from chitin.

2.2. Synthesis of ionic liquid (Tet-IL)

In a 150 mL flask, 5 mmol of 1-phenyl-1*H*-tetrazole-5-thiol and 5 mmol of (3-chloropropyl)trimethoxysilane (TMOS) were added to 50 mL of ethanol and the reaction mixture was subjected to reflux conditions. Reaction progress was followed by TLC. After 20 h, the reaction temperature was reduced to 50–55 °C. 5 mmol of 1,4-butane sultone were then added dropwise to the reaction mixture and stirring was continued for 8 h (Tet-IL).

2.3. Synthesis of CS@Tet-IL-Cu(II)

Firstly, in a 250 mL flask, 1.5 g of chitosan (CS) were added to Tet-IL, prepared in the previous stage, and the resulting mixture was refluxed for 24 h. When the reaction was over, the reaction mixture was cooled and the resulting precipitate (CS@Tet-IL) was separated from the reaction mixture by filtration, washed several times with ethanol, and then dried. In the next stage, in a 150 flask, a mixture of 1.2 g of CS@Tet-IL and 0.4 g of $CuCl_2$ was refluxed for 24 h. The resulting precipitate (CS@Tet-IL-Cu(II)) was then separated by filtration and dried after washing with ethanol (Scheme 3).

2.4. Synthesis of arylcyanamides

Different arylcyanamides were produced according to literature methods [39].

2.5. Synthesis of arylaminotetrazoles

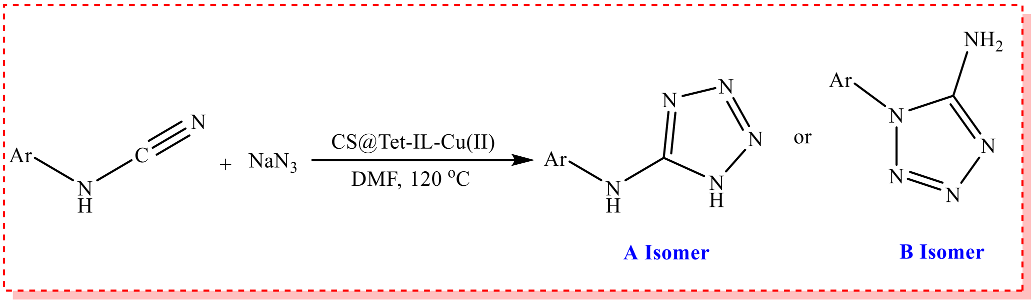
In a 50 mL flask, 1 mmol of arylcyanamides, 1.5 mmol of NaN_3, 0.05 g of CS@Tet-IL-Cu(II), and 7 mL of DMF were added and the mixture obtained was stirred at 120 °C for an appropriate time (the reaction progress was monitored by TLC). Upon the completion of the reaction, the reaction mixture was cooled and CS@Tet-IL-Cu(II) was removed from the reaction medium *via* filtration. The reaction mixture was then treated with 25 mL of HCl and 25 mL of ethyl acetate while being vigorously stirred. The organic layer was separated from the mixture and the aqueous layer was over-extracted using 25 mL of ethyl acetate. Finally, the separated organic layers were washed with water, followed by the removal of solvent, and crystallization in ethanol for further purification.

3. Results and discussion

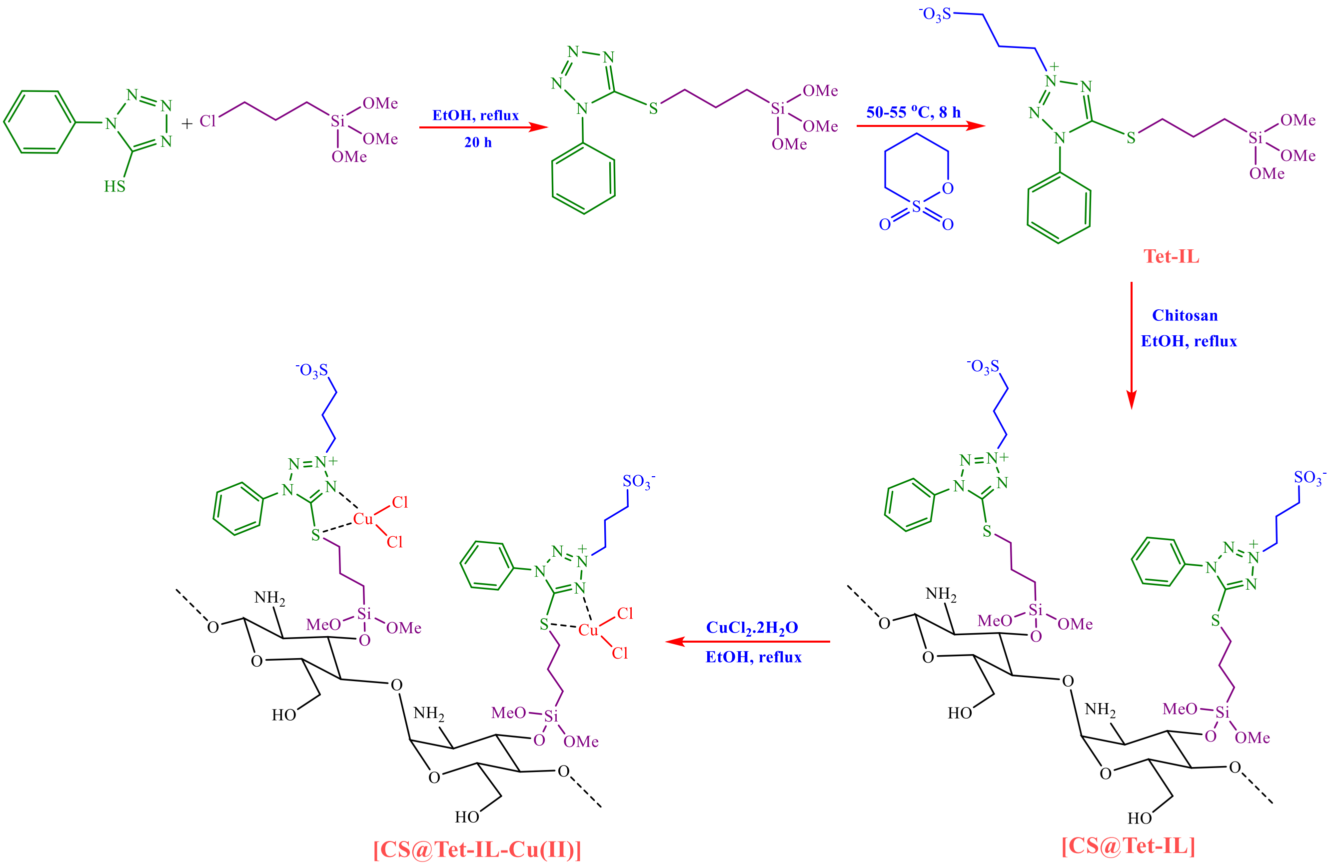
3.1. Characterization of CS@Tet-IL-Cu(II)

CS@Tet-IL-Cu(II) structure was confirmed using XRD, EDS, elemental mapping, TEM, STEM, FT-IR, ICP-MS and TG/DTA analyses. Fig. 2 displays the XRD pattern of CS@Tet-IL-Cu(II). The peak observed in $2\theta = 20°$ is related to the presence of chitosan in the synthesized catalyst, which matches the XRD pattern reported in the literature [40]. Due to the uniform distribution of copper particles in the synthesized catalyst, the peak corresponding to the copper particles is not visible.

The chemical compositions of CS@Tet-IL and CS@Tet-IL-Cu(II) were determined using EDS and elemental mapping analyses.



Scheme 2. Schematic representation of synthesis of arylaminotetrazoles using CS@Tet-IL-Cu(II).



Scheme 3. Synthetic pathway for the preparation of CS@Tet-IL-Cu(II) catalyst.

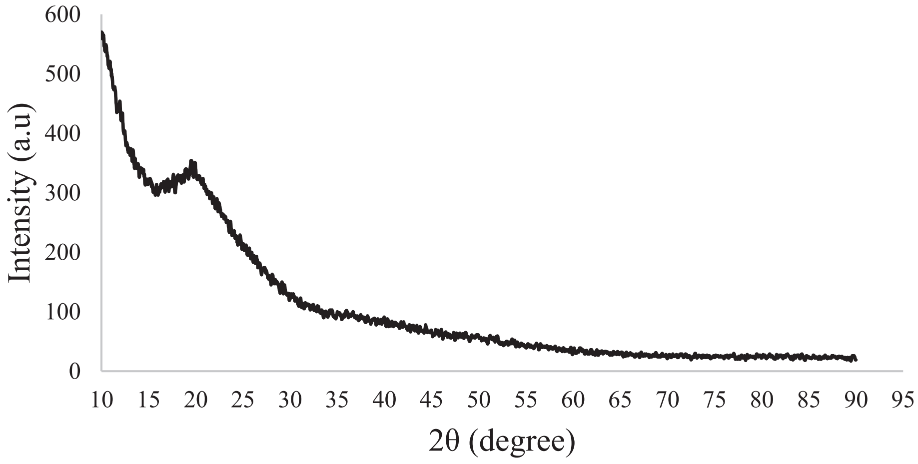
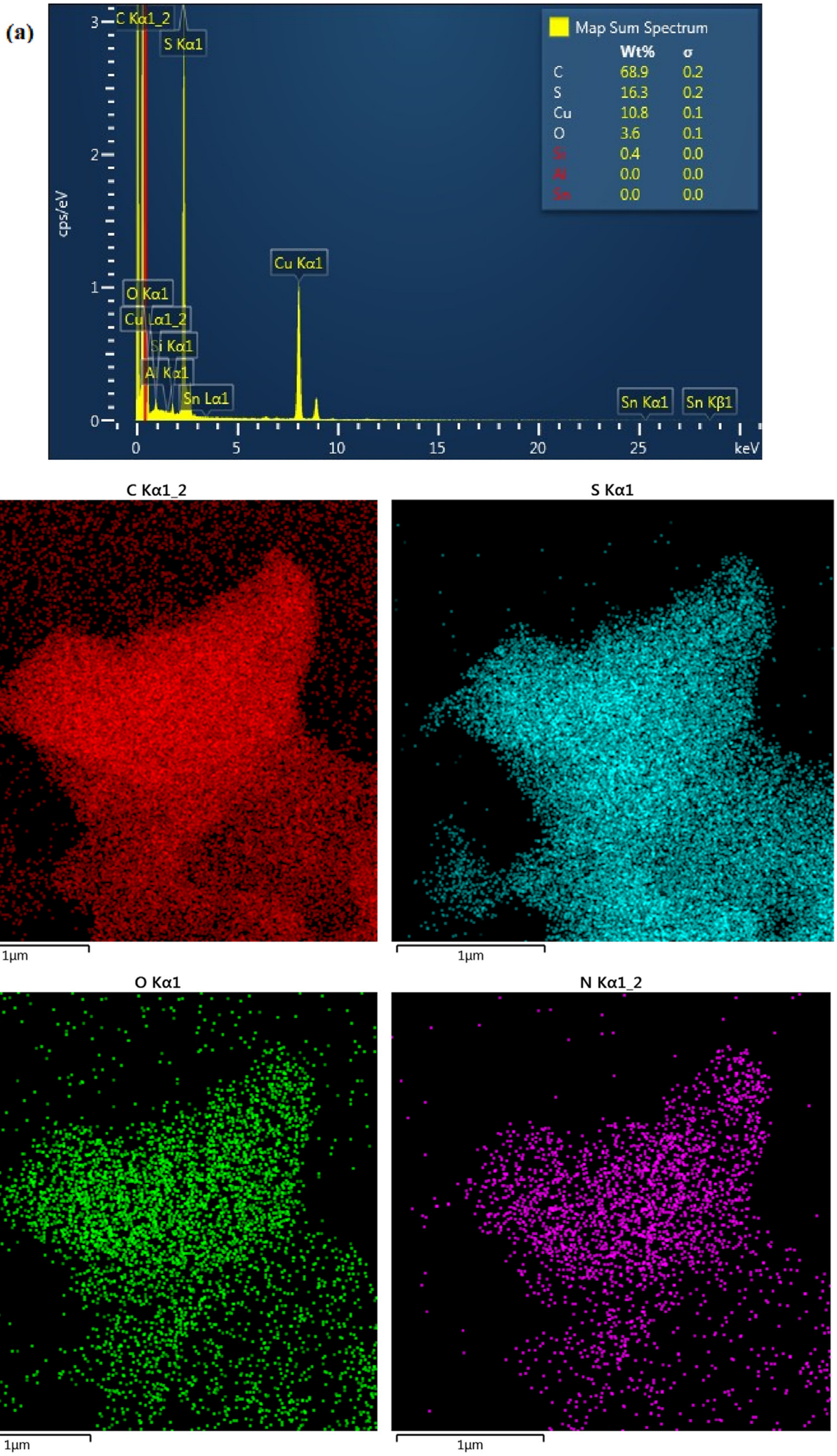


Fig. 2. XRD pattern of CS@Tet-IL-Cu(II).



🟨 Map Sum Spectrum

	Wt%	σ
C	68.9	0.2
S	16.3	0.2
Cu	10.8	0.1
O	3.6	0.1
Si	0.4	0.0
Al	0.0	0.0
Sn	0.0	0.0

Fig. 3. EDS spectra and elemental mapping analysis of a) CS@Tet-IL and b) CS@Tet-IL-Cu(II).

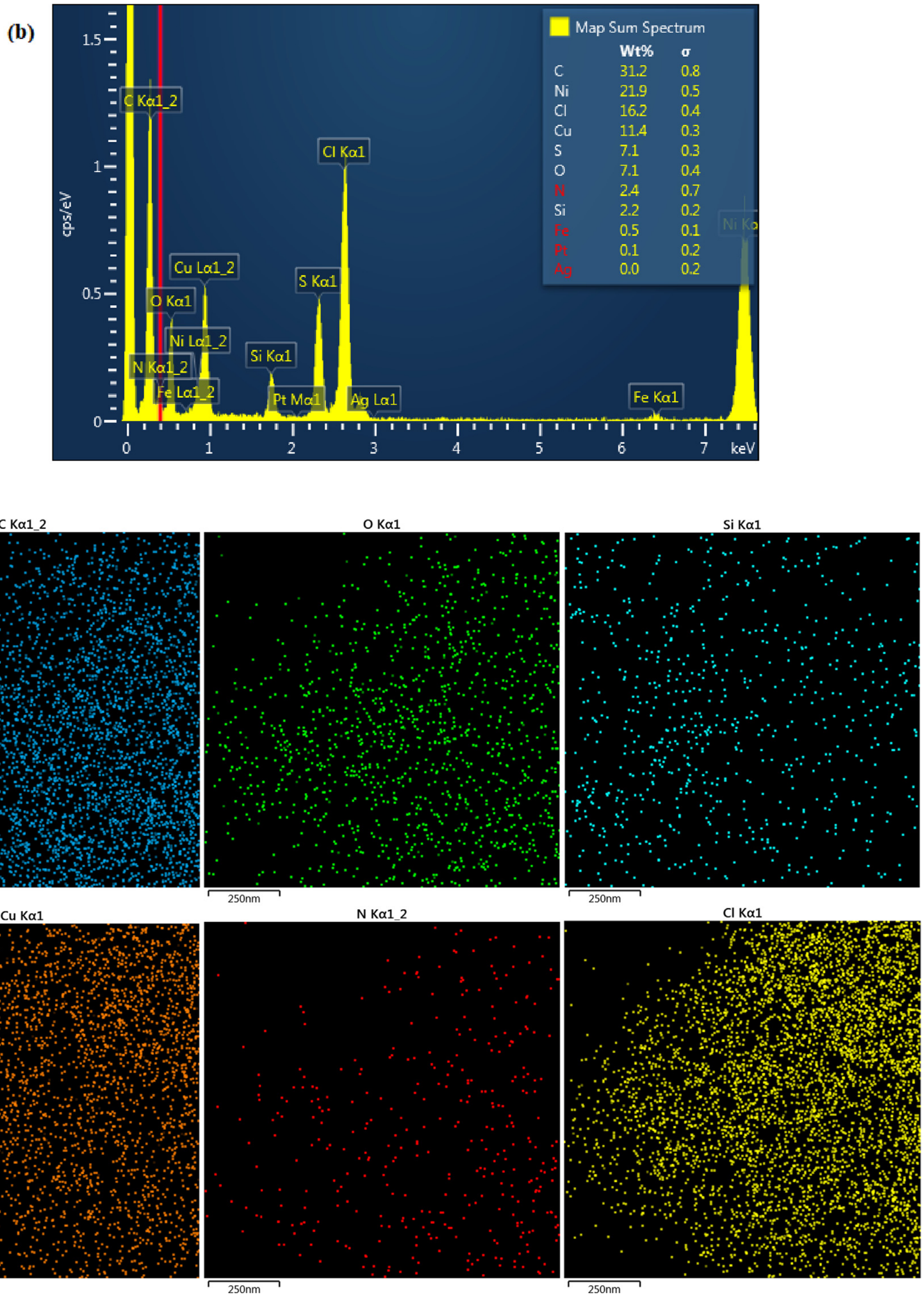


Fig. 3 (*continued*)

Fig. 3 displays the EDS spectra of the CS@Tet-IL and CS@Tet-IL-Cu (II). The EDS analysis of the catalyst was carried out by a Cu grid to hold the sample. As shown in Fig. 3 (a), copper is not observed in the CS@Tet-IL elemental mapping. EDS and elemental mapping of the CS@Tet-IL-Cu(II) confirmed the presence of the C, O, Si, Cu and N in the structure of CS@Tet-IL-Cu(II) (Fig. 3 (b)). The CS@Tet-IL-Cu(II) elemental mapping confirmed the uniform distribution of copper particles on the CS@Tet-IL surface. The content of the Cu within CS@Tet-IL-Cu(II), as determined using ICP-MS, was 0.6 wt%.

TEM analysis was applied to determine the particle size. Fig. 4 displays the TEM images of CS@Tet-IL and CS@Tet-IL-Cu(II). As shown in Fig. 4, the copper complex is evenly distributed on the surface of chitosan ionic liquid. The average size of a copper complex is about 10 nm. The STEM images of CS@Tet-IL and CS@Tet-IL-Cu(II) are displayed in Fig. 5, which confirm the homogenous assembly of the synthesized catalyst.

Fig. 6 shows the FT-IR spectra of CS@Tet-IL and CS@Tet-IL-Cu (II). As observed, the peak in the range of 3200–3500 cm^{-1} is related to NH and OH of chitosan. Furthermore, the peaks at

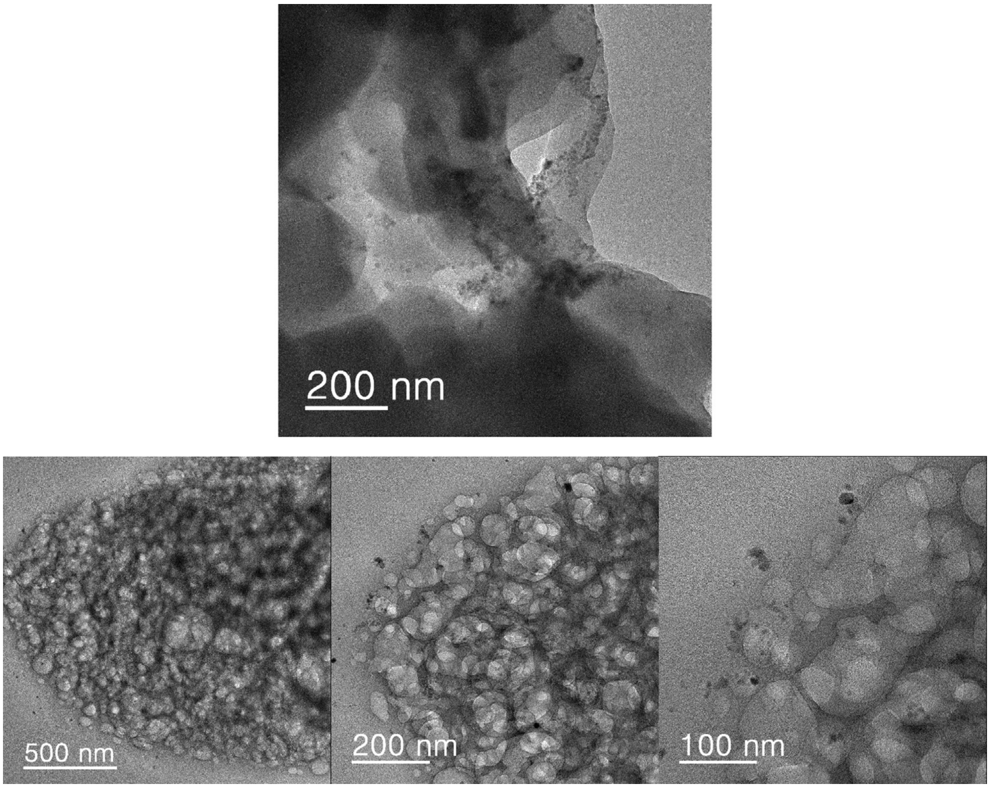


Fig. 4. TEM images of CS@Tet-IL (top) and CS@Tet-IL-Cu(II) (bottom).

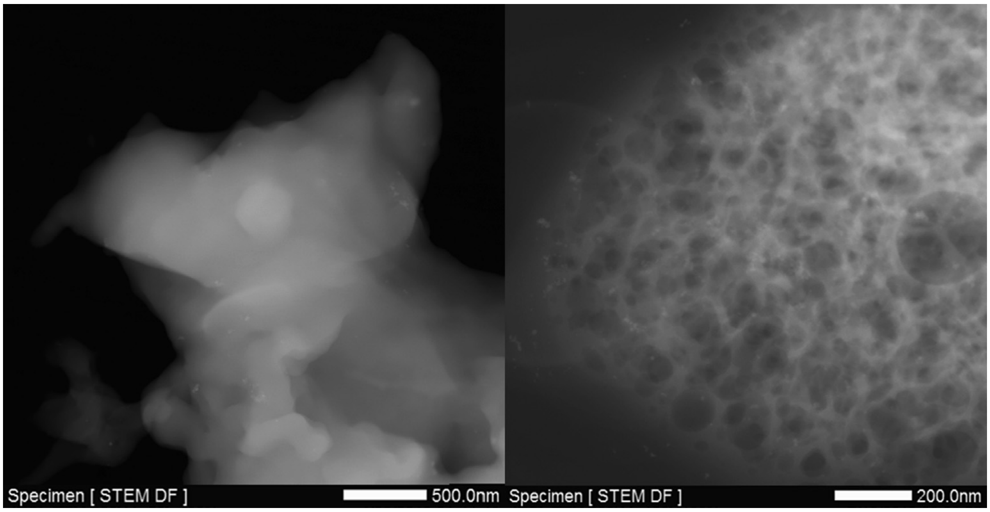


Fig. 5. STEM images of (left) CS@Tet-IL and (right) CS@Tet-IL-Cu(II).

2886, 1624 and 1152 cm^{-1} correspond to the tensile vibrations of C-H (sp^3) bonds, C = N bonds of tetrazole and SO^{3-}, respectively, which confirms the presence of tetrazole and IL in the structure of the synthesized CS@Tet-IL-Cu(II).

Thermogravimetric (TG) and differential thermal analysis (DTA) tests in airflow (120 mL/min) at a heating rate of 2 °C/min on an autonomic TG/DTA were carried out from 40 °C to 700 °C. Fig. 7 (a, b) shows the comparative weight loss of CS@Tet-IL and CS@Tet-IL-Cu(II). For both samples, the weight loss observed at temperatures below 200 °C is due to the release of water or organic solvents in the structure. In addition, in both samples, the weight loss in the temperature range of 200–500 °C corresponds to the

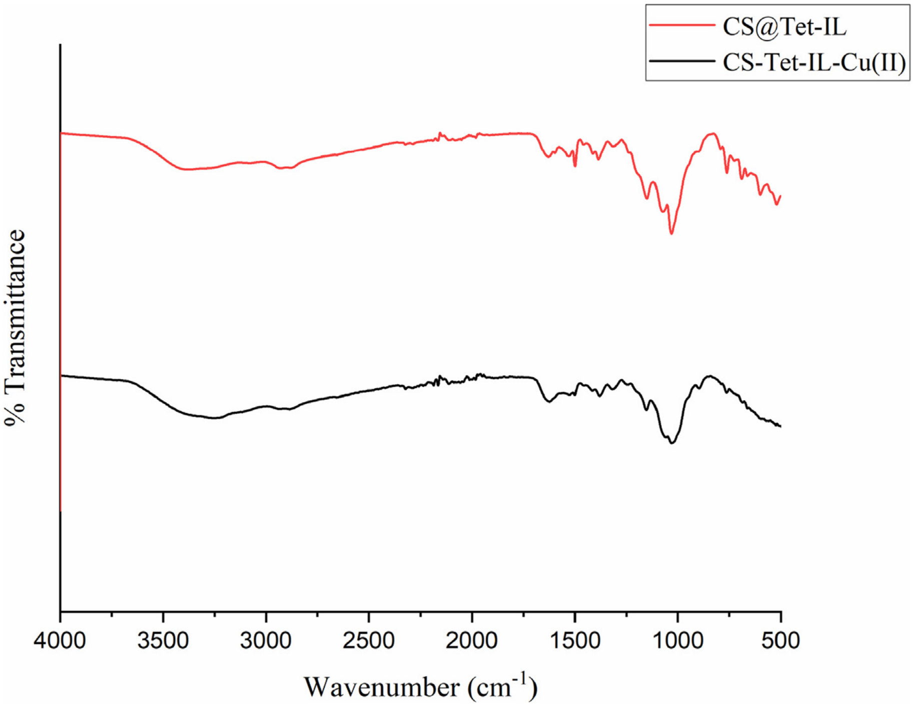


Fig. 6. FT-IR spectra of CS@Tet-IL and CS@Tet-IL-Cu(II).

decomposition of chitosan and 1-phenyl-1*H*-tetrazole-5-thiol functionalized ionic liquid. As shown in Fig. 7 (b), another decomposition stage is observed after 600 °C, which is related to the decomposition of the prepared catalyst.

3.2. Catalytic application of CS@Tet-IL-Cu(II) in the synthesis of arylaminotetrazoles

The synthesized CS@Tet-IL-Cu(II) was applied as an efficient catalyst in the [2 + 3] cycloaddition reaction of arylcyanamides and NaN_3 in DMF solvent for the synthesis of arylaminotetrazoles. The cycloaddition of 4-chlorophenylcyanamide and NaN_3 using CS@Tet-IL-Cu(II) was chosen as a model reaction to optimize the reaction conditions. Since cycloaddition reactions are performed at high temperatures, DMF was selected as the most suitable solvent. Different amounts of the catalyst were used to perform this reaction, the results of which are summarized in Table 1. The reaction does not occur in the absence of a catalyst (Table 1, entry 1). As displayed in Table 1, the most significant result is obtained in the reaction of 1 mmol of 4-chlorophenylcyanamide with 1.5 mmol of NaN_3 in the presence of 0.05 g of CS@Tet-IL-Cu(II) in DMF solvent (Entry 4). When the amount of catalyst is slightly increased, the product yield does not significantly increase (Entry 5). However, decreasing the amount of the catalyst significantly reduces the product yield (Entry 3).

To prepare arylaminotetrazoles, various types of arylcyanamides with electron donating and withdrawing groups were used (Table 2). Our results indicate that various arylcyanamides with different electron donating and withdrawing groups form arylaminotetrazole derivatives in high yields. In addition, the results show that cyanamides with electron donating groups are more reactive. On the other hand, as shown in Table 2, the cycloaddition reaction time of arylcyanamides containing electron-donating groups is shorter than that of arylcyanamides with electron withdrawing groups. According to Table 2, arylcyanamides containing electron withdrawing and donating groups produce isomer A (5-arylamino-1*H*-tetrazole) and isomer B (1-aryl-5-amino-1*H*-tetrazole), respectively.

The advantage of our method over other methods is that depending on the arylcyanamide used in the cycloaddition reaction, the product will be either isomer A or B, while other methods using HN_3, glacial acetic acid, and $FeCl_3$-SiO_2 yield an isomeric mixture (Scheme 4) [3,25]. In other words, our method is regiospecific. This is in concordance with the reports previously published regarding the synthesis of arylaminotetrazoles using natrolite zeolite, Ag/Fe_3O_4 nanocomposite, and Fe_3O_4@SiO_2-aminotet-Cu(II) catalyst [22–24]. The reported protocols have disadvantages such as the production of the mixtures of isomers [3,25], use of hydrazoic acid as a highly toxic and explosive compound, harsh reaction conditions, long reaction times, low yield, difficulty of work up due to the application of homogeneous catalysts, *in situ* generation of hydrazoic acid, difficulties in preparation and availability of the Natrolite zeolite [23] as a local and natural catalyst and also *Euphorbia peplus* Linn leaf extract for the synthesis of Ag/Fe_3O_4 nanocomposite [22]. Compared to other reported catalysts, CS@Tet-IL-Cu(II) avoids the previously reported problems and performs the best. To the best of our knowledge, this is the first report wherein an ionic liquid based tetrazole has been immobilized on the chitosan surface as an effective support.

Based on previous reports [22–24], a mechanism is proposed for the synthesis of arylaminotetrazole derivatives, as displayed in Scheme 5. The products were obtained *via* the guanidine azide intermediates.

The chemical structures of the synthesized arylaminotetrazoles derivatives (A and B isomers) were confirmed using FT-IR, ^{1}HNMR, and ^{13}CNMR spectroscopy (Fig. 8). In the FT-IR spectra of the synthesized A and B isomers, the peaks corresponding to NH and NH_2 are observed. In the ^{1}HNMR spectrum of A isomer, two NH peaks are observed corresponding to the NH of the amine connected to the aryl group and NH of the tetrazole ring. However, the ^{1}HNMR

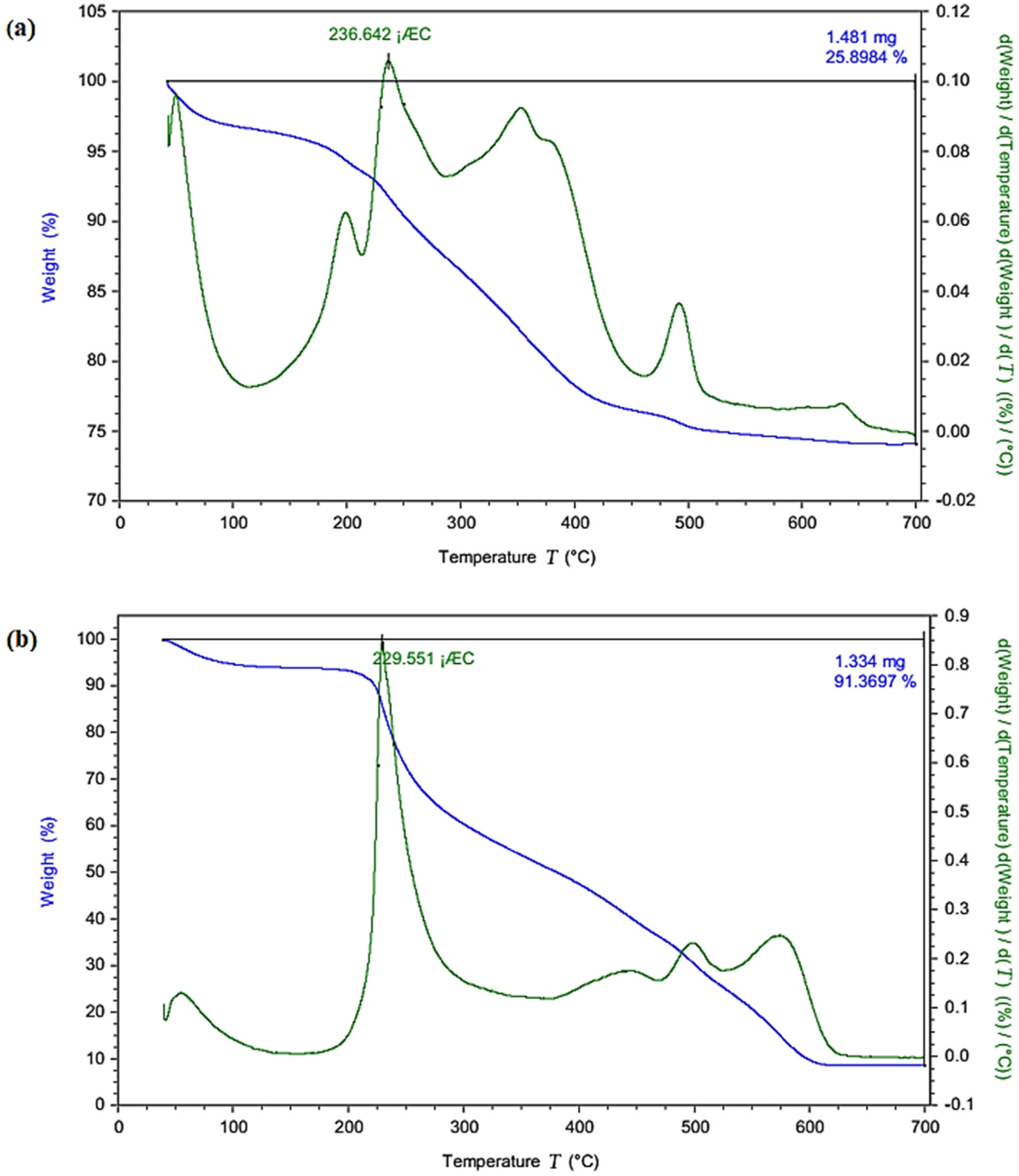


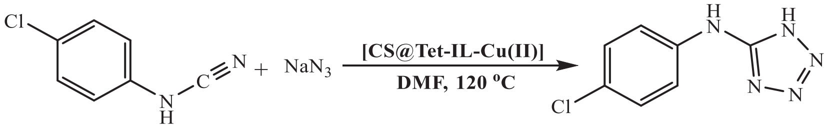
Fig. 7. TG/DTA analysis of (a) CS@Tet-IL and (b) CS@Tet-IL-Cu(II).

of B isomer shows one peak for the NH_2 group. Fig. 8 shows the ^{13}C-NMR spectrum of 5-(3-bromophenyl)amino-1*H*-tetrazole. As observed in the Figure; both isomers have peaks in the 154–158 region associated with the tetrazole ring.

3.3. Reusability of the CS@Tet-IL-Cu(II)

One of the significant features of heterogeneous catalysts is their ability to be recycled and reused. To test the recyclability of the catalyst, the cycloaddition reaction of 2-chlorophenylcyanamide with NaN_3 using CS@Tet-IL-Cu(II) in DMF solvent was selected as the model reaction. After the reaction is over; CS@Tet-IL-Cu(II) is separated from the reaction mixture by filtration, washed several times with ethanol, dried and applied for the next cycle. As shown in Scheme 6, CS@Tet-IL-Cu(II) can be used for up to 5 consecutive cycles with no significant reduction of catalytic performance. The XRD pattern, TEM images, and elemental mapping of the CS@Tet-IL-Cu(II) after 5 cycles display that the

Table 1
Optimization of reaction conditions for the synthesis of 5-(4-chlorophenyl)amino-1*H*-tetrazole.[a]



Entry	Catalyst (g)	Time (min)	Yield[b] (%)
1	0	120	0
2	0.01	60	66
3	0.03	40	78
4	0.05	30	85
5	0.07	30	85

[a] Reaction conditions: 4-chlorophenylcyanamide (1 mmol), NaN_3 (1.5 mmol), DMF (7 mL), catalyst, 120 °C.
[b] Isolated yield.

physical and chemical features such as chemical composition, size, and shape have not changed (Fig. 9). To check the heterogeneity of this catalyst, which is an important factor, the filtrate of each cycle was also analyzed by ICP-MS technique. Very low copper contamination was observed during these experiments. Copper leaching after the recycling tests was investigated and ICP-MS analysis showed that copper leaching was negligible (~0.1%).

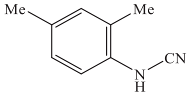
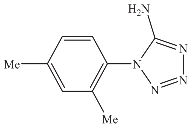
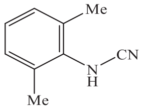
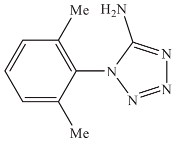
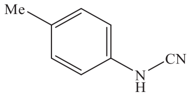
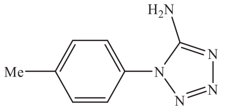
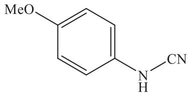
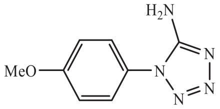
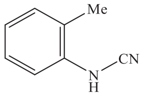
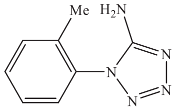
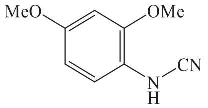
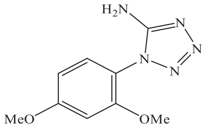
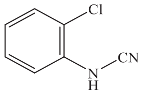
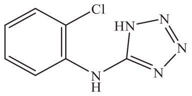
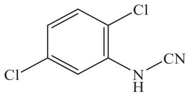
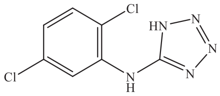
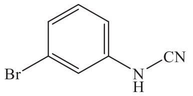
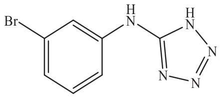
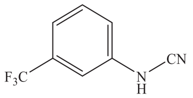
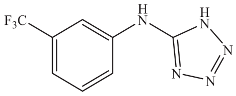
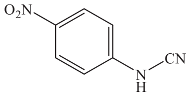
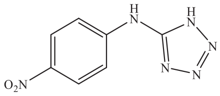
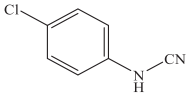
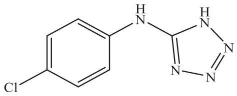
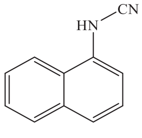
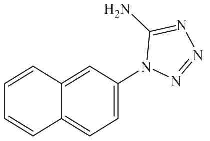
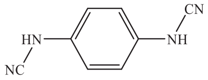
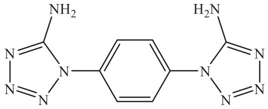
4. Conclusion

In this study, a chitosan supported metal ionic liquid has been successfully synthesized. Chitosan supported 1-phenyl-1*H*-tetrazole-5-thiol ionic liquid copper(II) complex has been prepared using (3-chloropropyl)trimethoxysilane (CS@Tet-IL-Cu(II)). The prepared CS@Tet-IL-Cu(II) has been applied as a novel and effective heterogeneous catalyst in the [2 + 3] cycloaddition reaction of arylcyanamides with NaN_3 in DMF as a solvent for the synthesis of arylaminotetrazole derivatives. The structure of the synthesized CS@Tet-IL-Cu(II) was confirmed using XRD, FT-IR, EDS, elemental mapping, STEM, TG/DTA, ICP-MS and TEM analyses. The prepared CS@Tet-IL-Cu(II) performs well in the synthesis of arylaminotetrazole derivatives even after 5 consecutive cycles. Our method for the synthesis of arylaminotetrazole derivatives is effective. It has many advantages such as the application of high performance heterogeneous catalysts, no use of toxic and explosive compounds such as NH_3, formation of high efficiency products, and single isomer (isomer A or B).

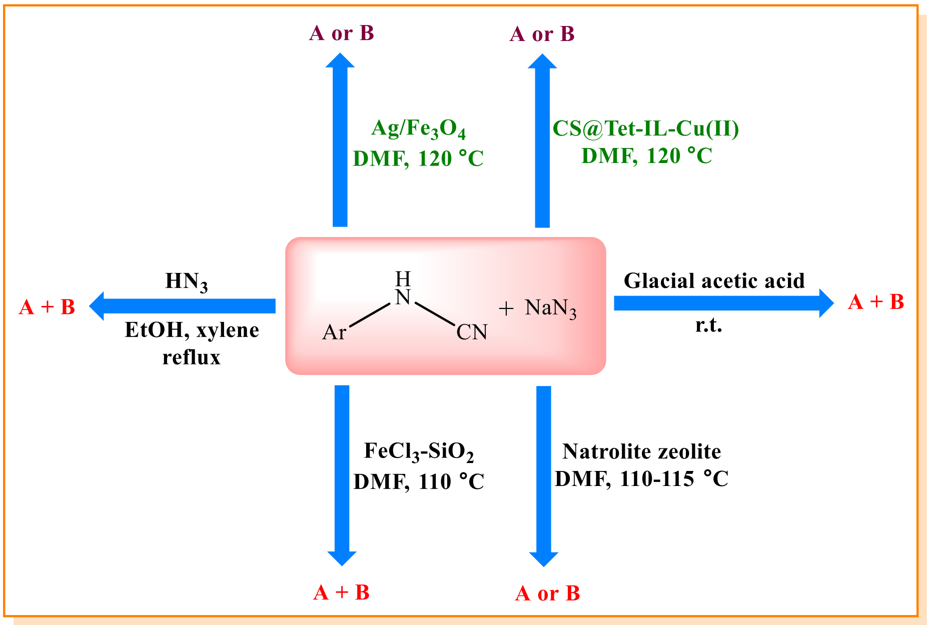
Declaration of Competing Interest

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.

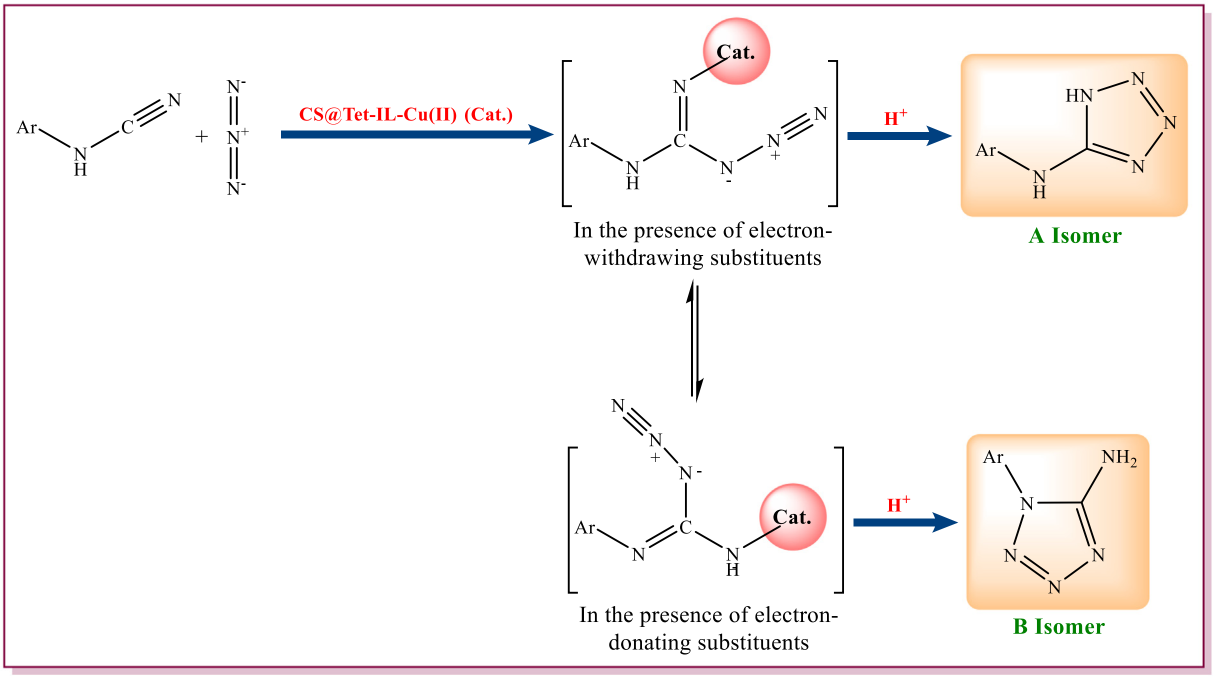
Table 2
Synthesis of arylaminotetrazole derivatives in the presence of CS@Tet-IL-Cu(II).[a]

Entry	Arylcyanamide	Product	Time (min)	Yield[b] (%)	TON	TOF (min^{-1})
1			20	86	182176	9109
2			25	83	175821	7033
3			20	83	175821	8791
4			20	82	173703	8685
5			20	85	180058	9003
6			20	86	182176	9109
7			30	83	175821	5860
8			40	81	171584	4289
9			30	85	180058	6002
10			45	85	180058	4001
11			45	83	175821	3907
12			30	85	180058	6002
13			20	86	182176	9109
14			20	85	180058	9003

[a] Reaction conditions: Arylcyanamide (1 mmol), NaN_3 (1.5 mmol), DMF (7 mL), CS@Tet-IL-Cu(II) (0.05 g), 120 °C.
[b] Isolated yield.



Scheme 4. Synthesis of 5-arylamino-1*H*-tetrazole (isomer A) and 1-aryl-5-amino-1*H*-tetrazole (isomer B) under different reaction conditions.



Scheme 5. The proposed mechanism for the synthesis of arylaminotetrazoles.

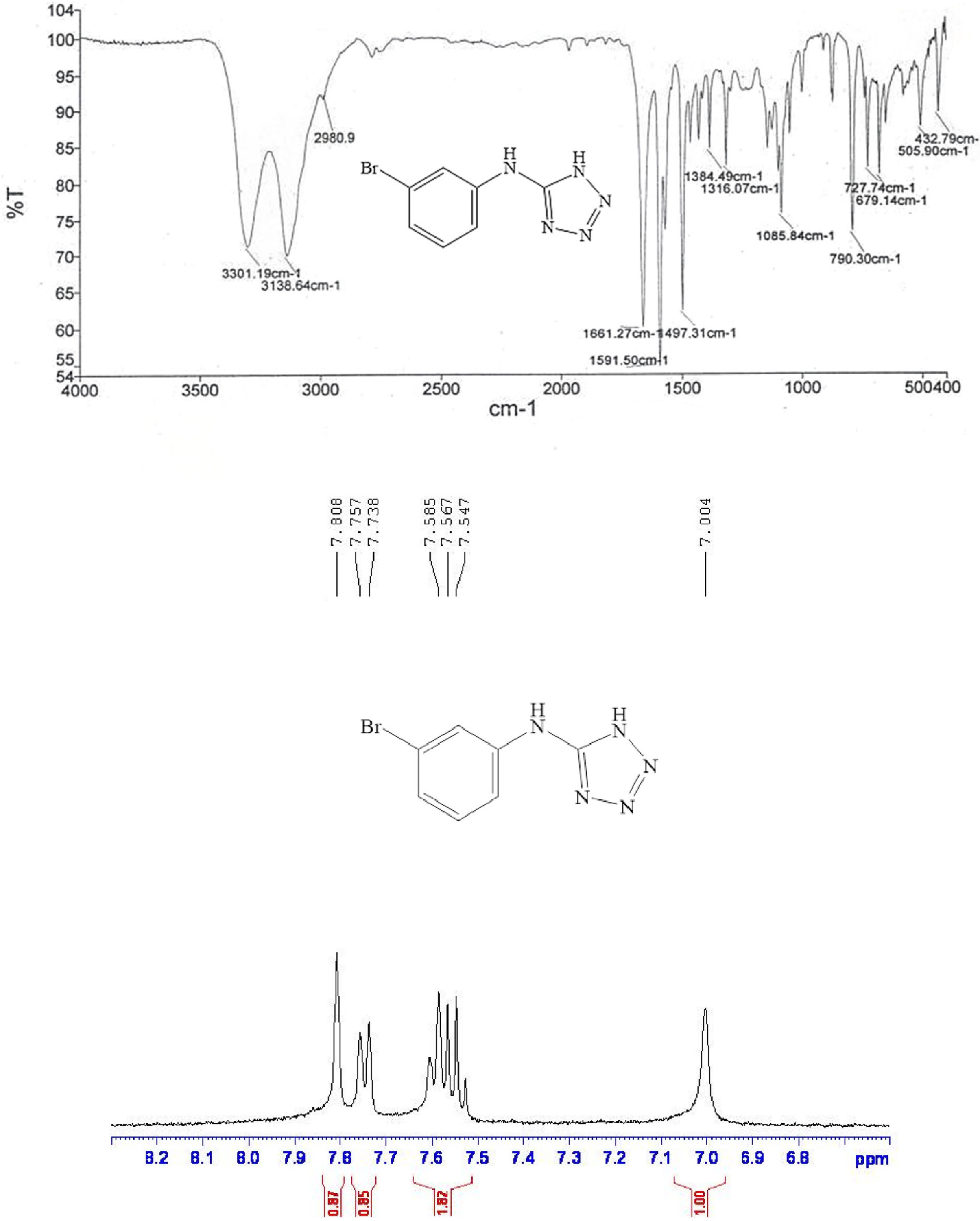


Fig. 8. FT-IR (top), ^{1}HNMR (center) and ^{13}CNMR (below) spectra of 5-(3-bromophenyl)amino-1*H*-tetrazole.

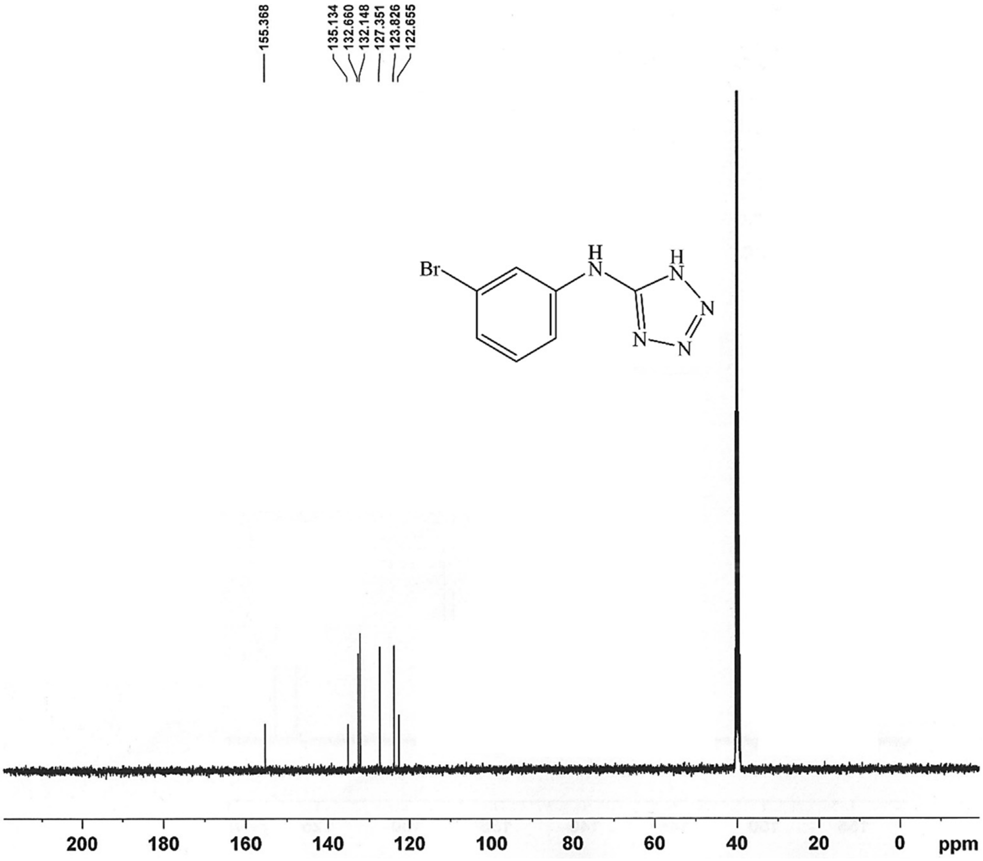
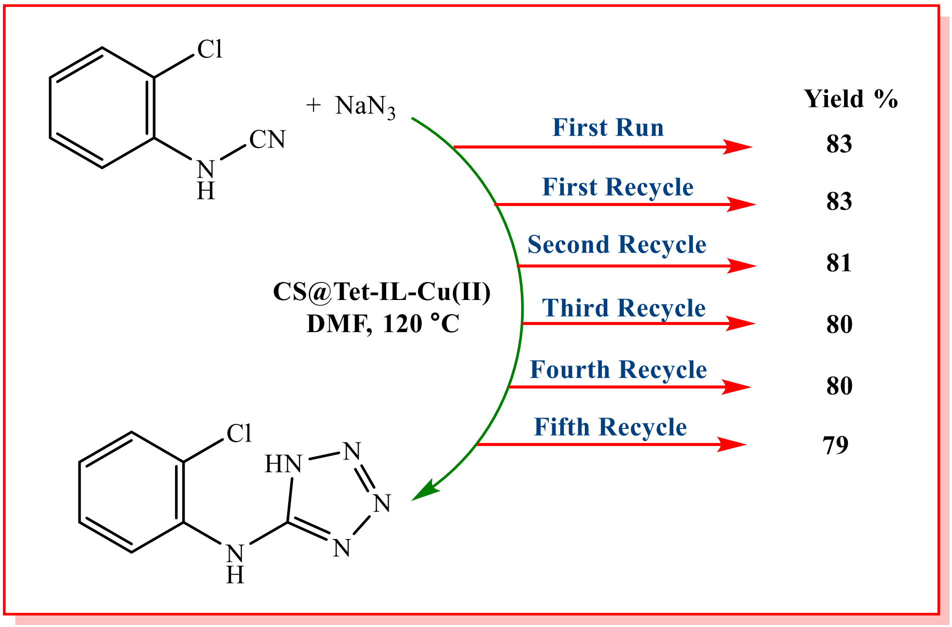


Fig. 8 (*continued*)



Scheme 6. Reusability of the CS@Tet-IL-Cu(II).

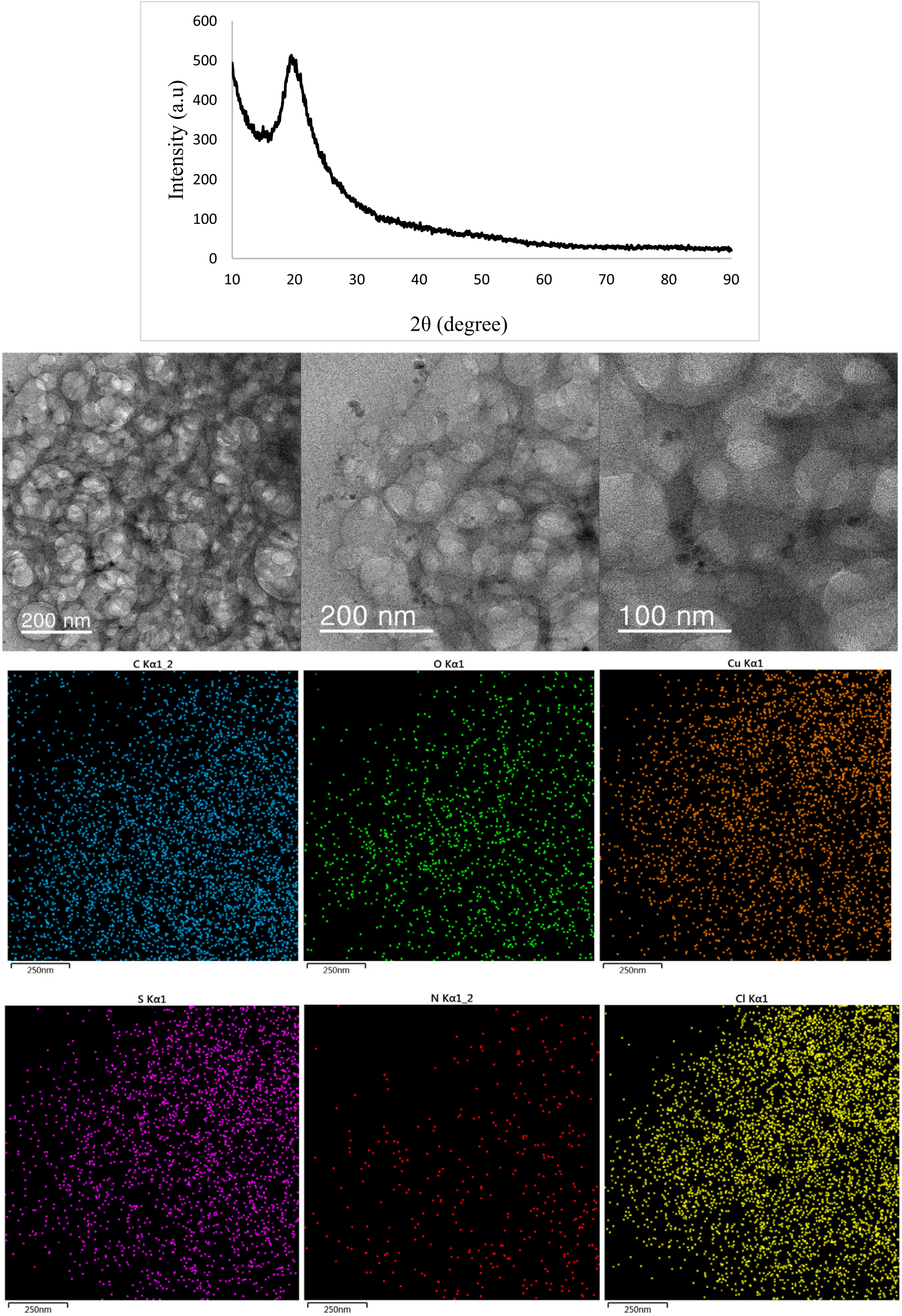


Fig. 9. XRD pattern, TEM images, and elemental mapping of the recycled CS@Tet-IL-Cu(II).

Acknowledgments

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References

[1] H. Zhao, Z.-R. Qu, H.-Y. Ye, R.-G. Xiong, In situ hydrothermal synthesis of tetrazole coordination polymers with interesting physical properties, Chem. Soc. Rev. 37 (1) (2008) 84–100.

[2] X.-M. Zhang, Y.-F. Zhao, H.-S. Wu, S.R. Batten, S. Weng Ng, Syntheses and structures of metal tetrazole coordination polymers, Dalt. Trans. (26) (2006) 3170, https://doi.org/10.1039/b518052j.

[3] A.R. Modarresi-Alam, M. Nasrollahzadeh, Synthesis of 5-arylamino-1*H* (2*H*)-tetrazoles and 5-amino-1-aryl-1*H*-tetrazoles from secondary arylcyanamides in glacial acetic acid: a simple and efficient method, Turk. J. Chem. 33 (2009) 267–280.

[4] Z.P. Demko, K.B. Sharpless, Preparation of 5-substituted 1*H*-tetrazoles from nitriles in water, J. Org. Chem. 66 (24) (2001) 7945–7950.

[5] T. Jin, F. Kitahara, S. Kamijo, Y. Yamamoto, Copper-catalyzed synthesis of 5-substituted 1*H*-tetrazoles via the [3+ 2] cycloaddition of nitriles and trimethylsilyl azide, Tetrahedron Lett. 49 (17) (2008) 2824–2827.

[6] C.-X. Wei, M. Bian, G.-H. Gong, Tetrazolium compounds: synthesis and applications in medicine, Molecules 20 (2015) 5528–5553.

[7] E.A. Popova, R.E. Trifonov, V.A. Ostrovskii, Tetrazoles for biomedicine, Russ. Chem. Rev. 88 (6) (2019) 644–676.

[8] V.A. Ostrovskii, R.E. Trifonov, E.A. Popova, Medicinal chemistry of tetrazoles, Russ. Chem. Bull. 61 (4) (2012) 768–780.

[9] B.S. Jursic, B.W. Leblanc, Preparation of tetrazoles from organic nitriles and sodium azide in micellar media, J. Heterocycl. Chem. 35 (1998) 405–408.

[10] Y.-T. Li, W.-Q. Yao, S. Zhou, J.-X. Xu, H. Lu, J. Lin, X.-Y. Hu, S.-K. Zhang, Synthesis, fungicidal activity, and 3D-QSAR of tetrazole derivatives containing phenyloxadiazole moieties, Bioorg. Med. Chem. Lett. 34 (2021) 127762.

[11] J. He, B. Li, F. Chen, Z. Xu, G. Yin, Tungstates: Novel heterogeneous catalysts for the synthesis of 5-substituted 1*H*-tetrazoles, J. Mol. Catal. A Chem. 304 (2009) 135–138.

[12] M.S. Pino-Gonzalez, A. Romero-Carrasco, S. Calvo-Losada, N. Oña-Bernal, J.J. Quirante, F. Sarabia, Synthesis of tetrazole fused azepanes and quantum chemical topology study on the mechanism of the intramolecular cycloaddition reaction, RSC Adv. 7 (79) (2017) 50367–50371.

[13] L.M.T. Frija, M.L.S. Cristiano, A. Gómez-Zavaglia, I. Reva, R. Fausto, Genesis of rare molecules using light-induced reactions of matrix-isolated tetrazoles, J. Photochem. Photobiol. C Photochem. Rev. 18 (2014) 71–90.

[14] D. Ichinari, A. Nagaki, J.-I. Yoshida, Generation of hazardous methyl azide and its application to synthesis of a key-intermediate of picarbutrazox, a new potent pesticide in flow, Bioorg. Med. Chem. 25 (23) (2017) 6224–6228.

[15] A.R. Modarresi-Alam, F. Khamooshi, M. Rostamizadeh, H. Keykha, M. Nasrollahzadeh, H.-R. Bijanzadeh, E. Kleinpeter, Dynamic ^{1}H NMR spectroscopic study of the restricted S-N rotation in aryl-*N*-(arylsulfonyl)-*N*-(triphenylphosphoranylidene) imidocarbamates, J. Mol. Struct. 841 (1–3) (2007) 61–66.

[16] B. Gutmann, T.N. Glasnov, T. Razzaq, W. Goessler, D.M. Roberge, C.O. Kappe, Unusual behavior in the reactivity of 5-substituted-1*H*-tetrazoles in a resistively heated microreactor, Beilstein J. Org. Chem. 7 (2011) 503–517.

[17] T. Tanaka, T. Okuda, Y. Yamamoto, Characterization of the CYP3A4 active site by homology modeling, Chem. Pharm. Bull. 52 (7) (2004) 830–835.

[18] S.M. Bayomi, M.A. Moustafa, A.R. Maarouf, M.H. Abutaleb, Design, synthesis, biological activity and molecular modeling of new heterocyclic tetrazole derivatives, J. Am. Sci. 12 (1) (2016) 40–56.

[19] R. Yella, N. Khatun, S.K. Rout, B.K. Patel, Tandem regioselective synthesis of tetrazoles and related heterocycles using iodine, Org. Biomol. Chem. 9 (9) (2011) 3235, https://doi.org/10.1039/c0ob01007c.

[20] P. Nimnual, J. Tummatorn, B. Boekfa, C. Thongsornkleeb, S. Ruchirawat, P. Piyachat, K. Punjajom, Construction of 5-aminotetrazoles via in situ generation of carbodiimidium ions from ketones promoted by $TMSN_3$/TfOH, J. Org. Chem. 84 (9) (2019) 5603–5613.

[21] N. Motahharifar, M. Nasrollahzadeh, A. Taheri-Kafrani, R.S. Varma, M. Shokouhimehr, Magnetic chitosan-copper nanocomposite: A plant assembled catalyst for the synthesis of amino-and *N*-sulfonyl tetrazoles in eco-friendly media, Carbohydr. Polym. 232 (2020) 115819.

[22] M. Sajjadi, M. Nasrollahzadeh, S. Mohammad Sajadi, Green synthesis of Ag/Fe_3O_4 nanocomposite using *Euphorbia peplus* Linn leaf extract and evaluation of its catalytic activity, J. Colloid Interface Sci. 497 (2017) 1–13.

[23] M. Nasrollahzadeh, D. Habibi, Z. Shahkarami, Y. Bayat, A general synthetic method for the formation of arylaminotetrazoles using natural natrolite zeolite as a new and reusable heterogeneous catalyst, Tetrahedron 65 (51) (2009) 10715–10719.

[24] M. Nasrollahzadeh, M. Sajjadi, H.A. Khonakdar, Synthesis and characterization of novel Cu(II) complex coated Fe_3O_4@SiO_2 nanoparticles for catalytic performance, J. Mol. Struct. 1161 (2018) 453–463.

[25] D. Habibi, M. Nasrollahzadeh, Silica-supported ferric chloride ($FeCl_3$-SiO_2): an efficient and recyclable heterogeneous catalyst for the preparation of arylaminotetrazoles, Synth. Commun. 40 (2010) 3159–3167.

[26] M. Maham, M. Khalaj, Synthesis of thiotetrazoles and arylaminotetrazoles using rutile TiO_2 nanoparticles as a heterogeneous and reusable catalyst, J. Chem. Res. 38 (8) (2014) 502–506.

[27] M. Ghasemi, A. Khataee, P. Gholami, R.D.C. Soltani, A. Hassani, Y. Orooji, In-situ electro-generation and activation of hydrogen peroxide using a CuFeNLDH-CNTs modified graphite cathode for degradation of cefazolin, J. Environ. Manage. 267 (2020) 110629.

[28] S. Sadjadi, M.M. Heravi, S.S. Kazemi, Ionic liquid decorated chitosan hybridized with clay: A novel support for immobilizing Pd nanoparticles, Carbohydr. Polym. 200 (2018) 183–190.

[29] M. Nasrollahzadeh, Z. Nezafat, N.S. Soheili Bidgoli, N. Shafiei, Use of tetrazoles in catalysis and energetic applications, Recent developments, Mol. Catal. 513 (2021) 111788.

[30] P. Mehdizadeh, Y. Orooji, O. Amiri, M. Salavati-Niasari, H. Moayedi, Green synthesis using cherry and orange juice and characterization of $TbFeO_3$ ceramic nanostructures and their application as photocatalysts under UV light for removal of organic dyes in water, J. Clean. Prod. 252 (2020) 119765.

[31] S.h. Jafari, S. Azizian, B. Jaleh, Adsorption kinetics of methyl violet onto TiO_2 nanoparticles with different phases, Colloids Surf. A Physicochem. Eng. Asp. 384 (1-3) (2011) 618–623.

[32] Y. Orooji, M. Ghanbari, O. Amiri, M. Salavati-Niasari, Facile fabrication of silver iodide/graphitic carbon nitride nanocomposites by notable photo-catalytic performance through sunlight and antimicrobial activity, J. Hazard. Mater. 389 (2020) 122079.

[33] Y. Orooji, R. Mohassel, O. Amiri, A. Sobhani, M. Salavati-Niasari, Gd_2ZnMnO_6/ZnO nanocomposites: green sol-gel auto-combustion synthesis, characterization and photocatalytic degradation of different dye pollutants in water, J. Alloys Compd. 835 (2020) 155240.

[34] P. Gholami, L. Dinpazhoh, A. Khataee, Y. Orooji, Sonocatalytic activity of biochar-supported ZnO nanorods in degradation of gemifloxacin: synergy study, effect of parameters and phytotoxicity evaluation, Ultrason. Sonochem. 55 (2019) 44–56.

[35] I.M.N. Vold, K.M. Vårum, E. Guibal, O. Smidsrød, Binding of ions to chitosan-selectivity studies, Carbohydr. Polym. 54 (4) (2003) 471–477.

[36] F. Xiao, F. Zhao, Y. Zhang, G. Guo, B. Zeng, Ultrasonic electrodeposition of gold-platinum alloy nanoparticles on ionic liquid-chitosan composite film and their application in fabricating nonenzyme hydrogen peroxide sensors, J. Phys. Chem. C 113 (3) (2009) 849–855.

[37] G. Aridoss, K.K. Laali, Highly efficient synthesis of 5-substituted 1*H*-tetrazoles catalyzed by Cu-Zn alloy nanopowder, conversion into 1,5- and 2,5-disubstituted tetrazoles, and synthesis and NMR studies of new tetrazolium ionic kiquids, Eur. J. Org. Chem. 2011 (31) (2011) 6343–6355.

[38] G.-H. Tao, Y. Guo, Y.-H. Joo, B. Twamley, J.M. Shreeve, Energetic nitrogen-rich salts and ionic liquids: 5-aminotetrazole (AT) as a weak acid, J. Mater. Chem. 18 (2008) 5524–5530.

[39] R.J. Crutchley, M.L. Nakicki, Pentaammineruthenium(III) complexes of neutral and anionic (2,3-dichlorophenyl)cyanamide: a spectroscopic analysis of ligand to metal charge-transfer spectra, Inorg. Chem. 28 (1989) 1955–1958.

[40] S. Kumar, J. Koh, Physiochemical, optical and biological activity of chitosan-chromone derivative for biomedical applications, Int. J. Mol. Sci. 13 (5) (2012) 6102–6116.