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FULL PAPER

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Copper(I)-chitin biopolymer based: An efficient and recyclable catalyst for click azide–alkyne cycloaddition reactions in water

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The naturally occurring α-chitin biopolymer was employed for the immobilisation of copper(I) ion, resulting into a new bioconjugate complex, namely, Cu(I)-α-chitin (CuI-CHT) with catalytic efficiency in copper-catalysed azide–alkyne cycloaddition reactions (click chemistry, CuAAC). The prepared catalyst was characterised by using spectroscopic and analytical methods such as Fourier-transform infrared (FT-IR), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), X-ray diffraction (XRD) and inductively coupled plasma (ICP) analysis. The catalytic activity of CuI-CHT was investigated in the [3 + 2] cycloaddition reactions of alkynes and organic azides for the regioselective click of 1,4-disubstituted-1,2,3-triazole derivatives in water at room temperature. The catalytic results indicate that the prepared CuI-CHT catalyst led to a high yield with a regioselective synthesis of the corresponding 1,4-disubstituted-1,2,3-triazoles under strict click conditions. The reusability and simple recovery of this catalyst make it a suitable sustainable catalyst for CuAAC reactions.

KEYWORDS
1,4-disubstituted-1,2,3-triazoles, click chemistry, DFT calculations, heterogeneous catalysis, regioselectivity, α-chitin

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1 | INTRODUCTION

1,2,3-Triazole moieties are an important class of organic compounds which have many applications in biology,[1] materials science[2] and medicinal chemistry.[3] As for their preparation, the most straightforward method for the formation of 1,2,3-triazole derivatives is the established click chemistry copper-catalysed azides–alkynes [3 + 2] cycloaddition (CuAAC) reaction.[4] The original noncatalysed side of the azide–alkyne [3 + 2] cycloadditon reaction, known as Huisgen reaction, has been characterised by its slow rate and low selectivity due to the high reaction kinetic barrier. The discovery of CuAAC improved the regioselectivity of the [3 + 2] cycloaddition reaction of azides and alkynes, by selectively affording 1,4-disubstitued-1,2,3-triazoles in an efficient way and easy manner from a wide range of azide and alkynes substrates.[5,6] A variety of homogeneous and heterogeneous catalytic systems for CuAAC reactions has been used for the click of 1,4-disubstitued-1,2,3-triazole derivatives.[7–13] In recent years, increasing efforts have been devoted to the use of eco-friendly polymer supports for the metal catalysts in view of obtaining heterogeneous catalysts that can be recovered and recycled.[14–16] In this context, naturally occurring polysaccharides such as cellulose, chitosan and alginate biopolymers have been employed as biosupports for the stabilisation of copper ions followed by their application for the regioselective synthesis of 1,4-disubstituted-1,2,3-triazoles under the click chemistry approach (Chart 1).[17–21]

We herein present the use of the α-chitin biopolymer as support for the preparation and characterisation of copper(I)-chitin-based catalyst (CuI-CHT) and its application in the click chemistry reaction between a variety of alkynes and azides in water as solvent. The obtained catalyst was studied in the click of the corresponding 1,4-disubstituted-1,2,3-triazoles in a regioselective manner. The separation from the reaction mixture through simple filtration, recovery of reuse of this catalyst has also been addressed.

2 | EXPERIMENTAL SECTION

2.1 | Materials and methods

α-Chitin was obtained from shrimp shells (*Parapenaeus longirostris*) following the detailed procedures described previously.[22] Copper(I) iodide, $MgSO_4$ and all the other reagents were purchased from Sigma-Aldrich. The obtained α-chitin and the CuI-CHT supported catalyst were characterised using several methods. X-ray diffraction (XRD) patterns were recorded on a diffractometer (Rigaku SmartLab), which operated at 40 kV and 30 mA utilising copper anode ($K_\alpha = 1.5418$ Å). The XRD data were collected in the 2θ range 5° to 70° with a scanning step size of 0.02°. Scanning electron microscopy (SEM) observations of the samples surface were performed using a TESCAN-VEGA3 microscope under an accelerating voltage of 20 kV. The specific elemental composition was determined by an energy-dispersive X-ray (EDX) analyser. The functional groups were identified by using a Bruker VERTEX 70 spectrometer, which was operated at room temperature at 4 cm^{-1} over a range of 4000–400 cm^{-1}. A TA–TGA55 Thermogavimetric Analyser was used to evaluate the thermal stabilities of the samples under a nitrogen flow from 30°C to 600°C with a heating rate of 10°C min^{-1}. ^1H NMR and ^{13}C NMR were recorded on a Bruker DRX-300 spectrometer. Inductively coupled plasma (ICP) (iCAP 6000) analysis was used to determine the copper loading.

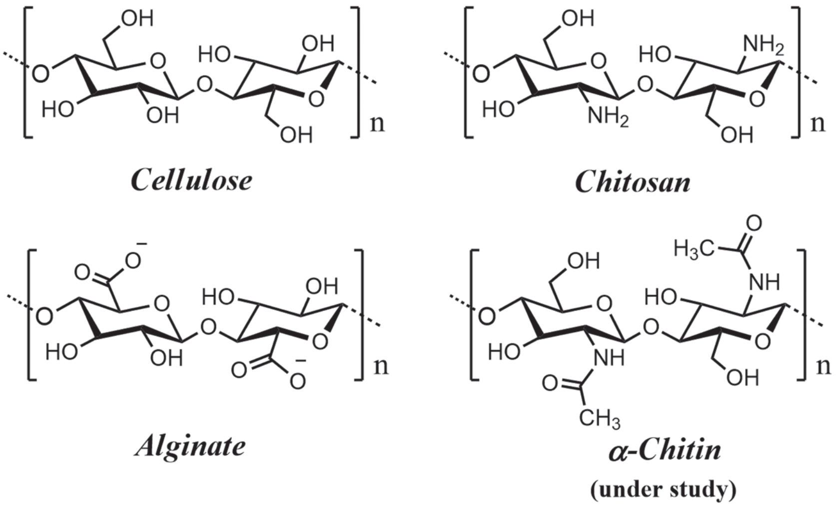


CHART 1 Naturally occurring polysaccharides

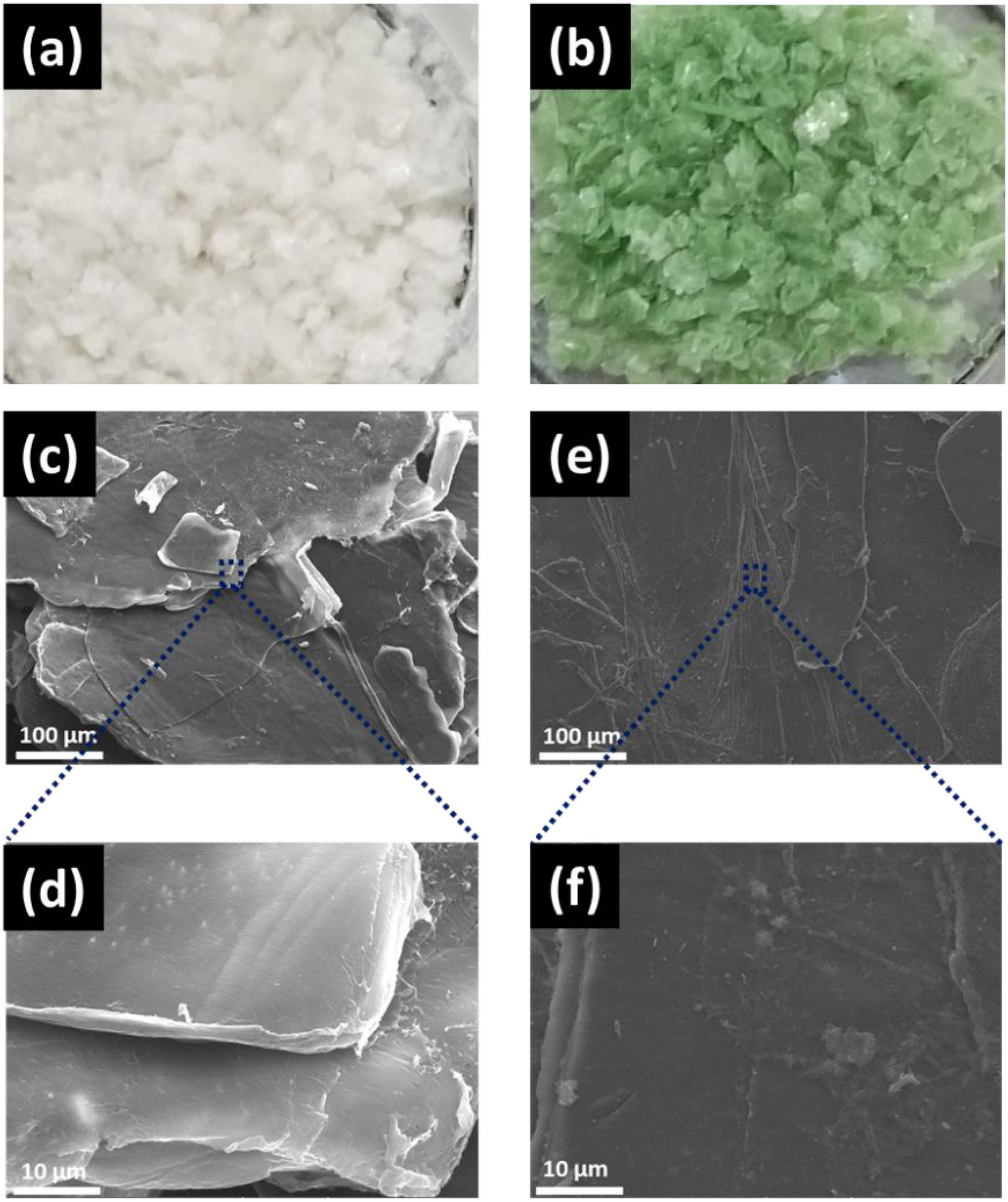


FIGURE 1 Photographs of (a) α-chitin (CHT) and (b) CuI-CHT catalyst and surface scanning electron microscopy (SEM) images of (c,d) CHT and (e,f) CuI-CHT catalyst at different scales

2.2 | Preparation of the CuI-CHT supported catalyst

Natural α-chitin (0.5 g), 0.125 g (0.66 mmol) of copper(I) iodide and 10 cm^3 of acetonitrile were introduced into a well-dried 25-cm^3 bottom flask. The mixture was stirred under stirring for 12 h. The catalyst was filtered, washed with acetonitrile (2 × 15 cm^3) and dried under vacuum overnight. According to the ICP analysis, the copper content in the prepared catalyst was estimated to be 6.58% (w/w).

2.3 | General procedure: Synthesis of 1,2,3-triazole from azide and alkyne

Alkyne (0.5 mmol) and azide (0.6 mmol) were added to a suspension of CuI-CHT (4 mg, 1 mol% Cu) in H_2O

(3 cm^3). The reaction mixture was kept under continuous stirring until the completion of the reaction. Then, the mixture was diluted by dichloromethane and the catalyst was recovered through simple filtration. It was then washed and dried for its reuse in subsequent runs. The organic phase was removed under vacuum to isolate the corresponding pure 1,2,3-triazole derivative.

2.4 | General procedure for one-pot synthesis of 1,4-disubstituted-1,2,3-triazoles

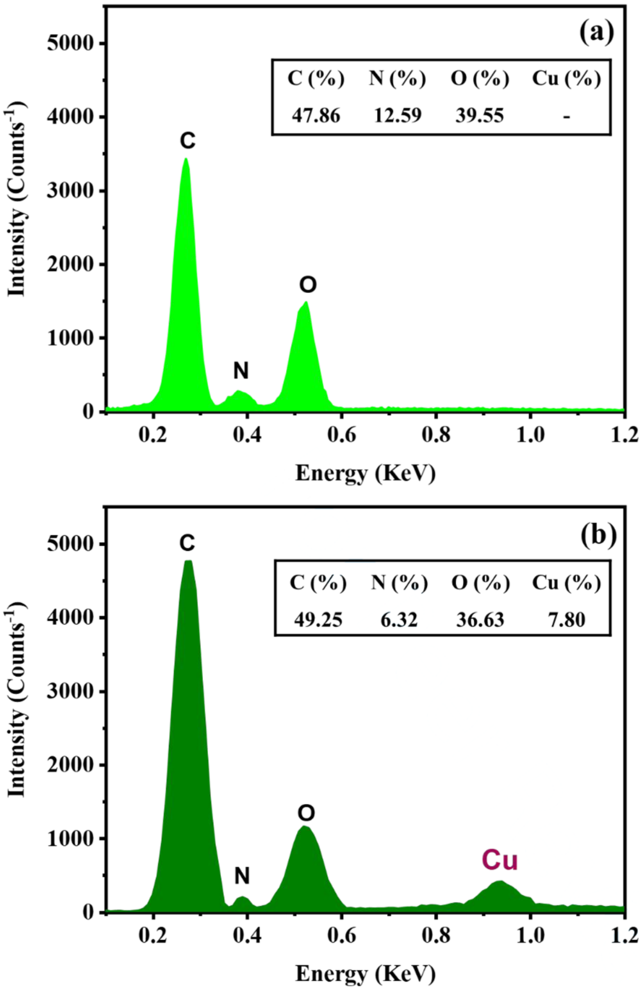
Alkyl halide (0.6 mmol), alkyne (0.5 mmol) and NaN_3 (0.6 mmol) were added to a suspension of CuI-CHT (8 mg, 2 mol% Cu) in H_2O (5 cm^3) and then stirred for 24 h at room temperature. Further, the product was extracted by using dichloromethane and then filtered off to separate the CuI-CHT catalyst. The corresponding pure 1,4-triazole derivative was obtained after the evaporation of the organic solvent under vacuum.

3 | RESULTS AND DISCUSSION

3.1 | Characterisation of the CuI-CHT catalyst

The optical photomicrographs and SEM images of the α-chitin (CHT) and CuI-CHT catalysts are shown in Figure 1. After the adsorption process of copper into the α-chitin surface, there is a change in the colour of the CHT from white to green as shown in Figure 1a,b. This change in colour could be due to the significant amount of copper adsorbed on the CHT surface. In general, the SEM images show that the adsorption of copper on the surface of α-chitin is accompanied by a change in the morphological structures. The SEM images in Figure 1c,d confirm that CHT presents a flat and regular crystalline surface and that it is made of flakes of different sizes. Furthermore, the SEM images of the CuI-CHT surface show a uniform surface morphology and dense fibrils and roughness without much porosity. However, the surface appears to be less crystalline (Figure 1e). At the highest magnification (Figure 1f), the CuI-CHT surface loses its crystalline appearance, but some attached particles can still be observed.

The differences observed in the morphological surfaces of the native α-chitin and the prepared CuI-CHT catalyst are confirmed by an EDX elemental analysis, which shows a peak around 0.95 keV corresponding to the Cu (7.80%) which appears after adsorption (Figure 2). Furthermore, the presence of major α-chitin element constituents such as oxygen (O), carbon (C) and nitrogen (N) confirms that the supported catalyst maintains the elemental composition of α-Chitin. Furthermore, the absence of a peak corresponding to the other elements indicates the absence of any impurity in the sample.



C (%)	N (%)	O (%)	Cu (%)
47.86	12.59	39.55	-

C (%)	N (%)	O (%)	Cu (%)
49.25	6.32	36.63	7.80

FIGURE 2 Energy-dispersive X-ray (EDX) spectra of (a) α-chitin and (b) CuI-CHT catalyst

In order to get deeper insights about the spatial distribution of elements on the surface of the CuI-CHT catalyst, the elemental mapping was employed by using EDX (Figure 3). The copper mapping image (Cu) shows a homogeneous distribution on the CuI-CHT catalyst surface. Furthermore, the elemental mapping analysis demonstrates that nitrogen (N) and copper (Cu) are almost completely interloped with each other. This result indicates that the acetamide groups in α-chitin promote the distribution of copper on the surface, this feature allowing to better predict the catalytic activity of the developed CuI-CHT catalyst.

XRD was employed to compare α-chitin with α-chitin loaded copper(I) iodide (Figure 4). As shown in a previous report,[23] α-chitin monomers undergo strong intermolecular hydrogen bonds, enabling α-chitin to exhibit

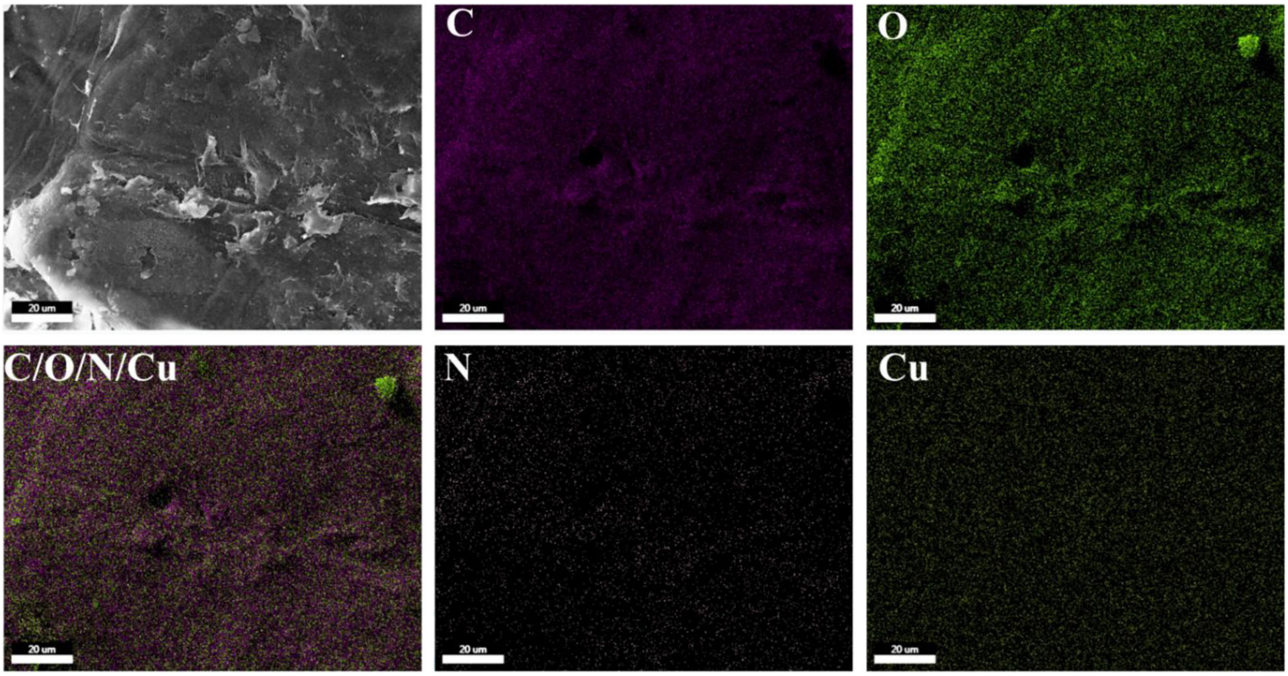


FIGURE 3 Energy-dispersive X-ray (EDX) mapping of the prepared CuI-CHT catalyst

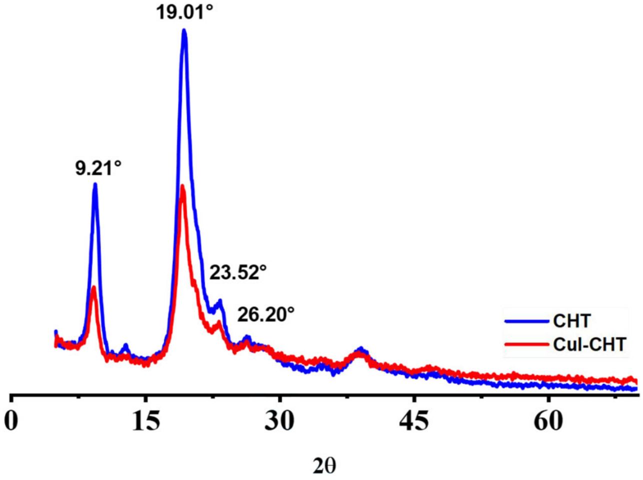


FIGURE 4 X-ray diffraction patterns of α-chitin (CHT) and CuI-CHT catalyst

more crystalline polymorph character compared with other chitin forms (β-chitin and γ-chitin) because of its antiparallel compact structure. In this study, the XRD patterns of CHT showed diffraction peaks at 9.21°, 19.01°, 23.52° and 26.20°, which are characteristic of the α-chitin form.[24] The same peaks are observed in the XRD patterns of the CuI-CHT catalyst, which has lower peak intensities but similar peak positions. Also, a non-copper peak was observed. This result can be explained by the small Cu particles present in α-chitin which do not form a long-range ordering, preventing the XRD diffraction from being detected.[25] The lower peak intensities on the other hand can be explained by the lowering of the amount of free acetyl groups during the coordination to copper, which leads to the deformation of hydrogen bonds and decreases the degree of crystallinity of the CuI-CHT.[26]

The thermal stability of the CHT and the prepared CuI-CHT catalysts was investigated through a thermogravimetric analysis (TGA) under nitrogen flow. This analysis shows the occurrence of two mass loss stages (Figure 5). The first stage occurred between 44°C and 120°C, with weight losses for CHT and CuI-CHT of 5.08% and 3.18%, respectively. This weight loss corresponds to the evaporation of physically adsorbed water. The second stage occurred between 260°C and 420°C with a weight loss of 95.55% for the native α-chitin, which is significantly greater than the 85.06% weight loss of the CuI-CHT catalyst. The decomposition of the α-chitin structure chains account for these weight losses.[23] The decomposition of the developed catalyst did not occur below 250°C. This feature illustrates the potential of the application of the α-chitin catalysts because the thermal stability of catalysts is needed for several heterogeneous catalytic reactions.[27]

A Fourier-transform infrared (FT-IR) analysis was conducted to assess the purity of the extracted α-chitin and to observe if there is a structural change after the copper loading. As shown in the FT-IR spectrum of the -CuI-CHT catalyst, all the bands are almost the same of those for the pure α-chitin, which indicates that no chemical modification occurred (Figure 6). An examination of

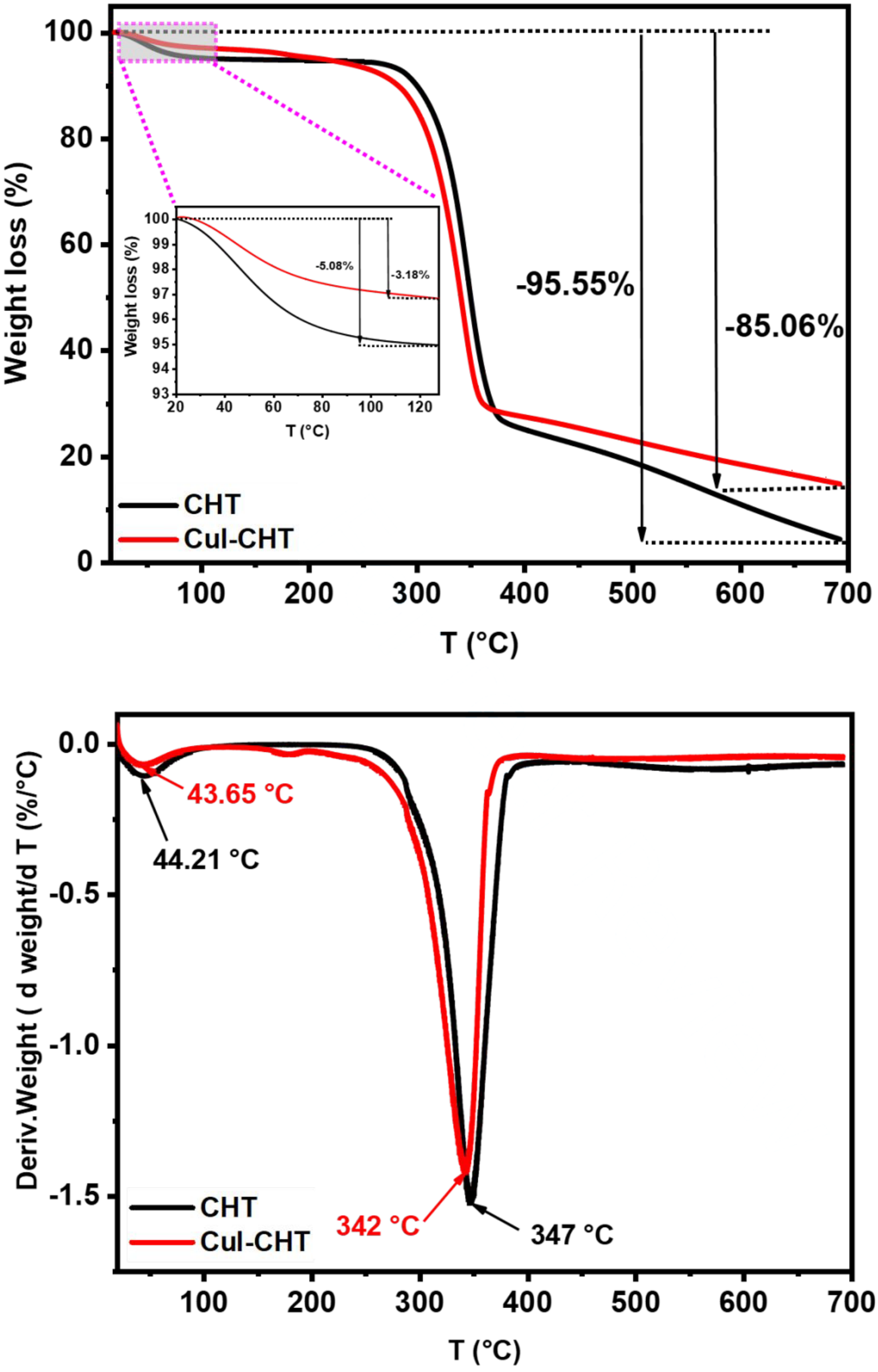


FIGURE 5 Thermo gravimetric analysis (TGA)/differential thermogravimetry (DTG) of the α-chitin (CHT) and the CuI-CHT catalyst

the FT-IR spectrum of both the α-chitin and the CuI-CHT catalysts shows stretching vibrations of hydroxyl groups around 3400 cm^{-1}.[22,25,28] Intrachain and interchain hydrogen bonds and the NH stretching of α-chitin at 3268 and 3109 cm^{-1} are also present.[29,30] The other characteristic bands located at 2890 and 2967 cm^{-1} are assigned to the C—H stretchings of the CH_2 and CH_3 groups.[25] The most prominent change in the FT-IR spectrum of CuI-CHT was a slight shift in the position of the peaks, which can be attributed to the C═O vibration of amide I and amide II to 1660, 1632 and 1558 cm^{-1}, respectively[31] (Figure 6). The second

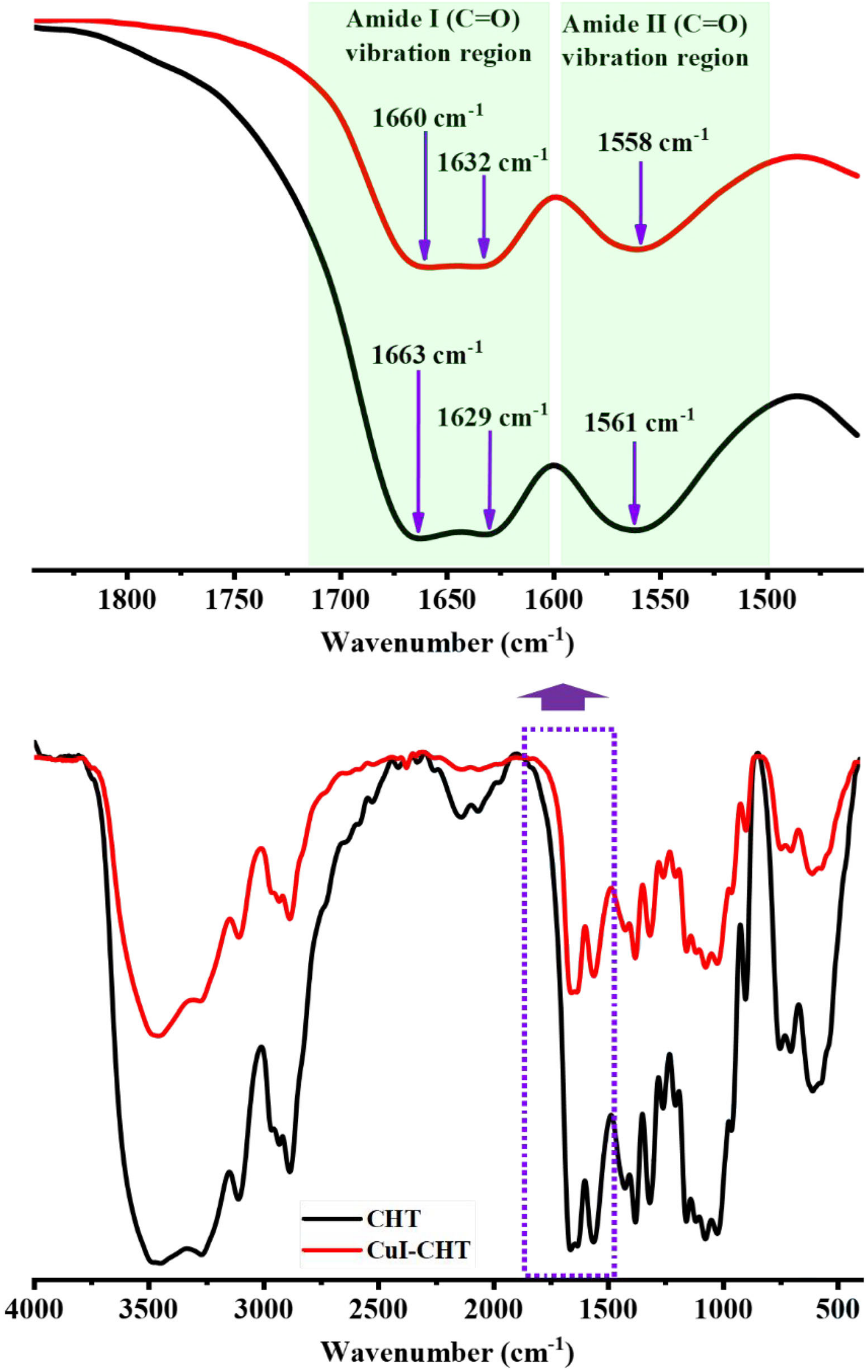


FIGURE 6 Fourier-transform infrared (FT-IR) spectra of the α-chitin (CHT) and the CuI-CHT catalyst

difference in the FT-IR spectrum of CuI-CHT compared with α-chitin is the reduction in the intensities of the peaks, which is attributed to the anchoring of copper on the α-chitin surface.

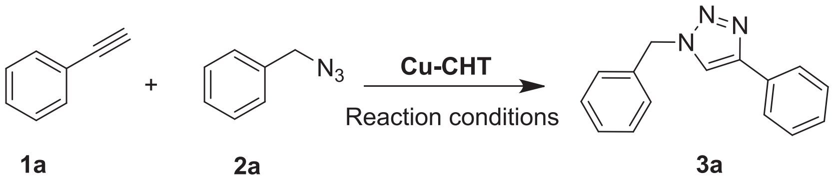
3.2 | Catalytic study

To evaluate the efficiency of the newly synthesised catalyst, it was tested in [3 + 2] cycloaddition reactions between terminal alkynes and organic azides. In the present work, the reaction between phenyl acetylene (**1a**) and benzyl azide (**2a**) in water as solvent was chosen as the model reaction (Scheme 1). Different reaction conditions, such as different copper sources and the amount of a catalyst were investigated in the studied reaction, using the CuI-CHT catalyst (Table 1). The controlled experiments show that the [3 + 2] cycloaddition azide–alkyne reaction does not take place in the absence of the catalyst (Entries 1 and 2). The use of copper(I) iodide only leads to a moderate yield of the corresponding 1,4-triazole (**3a**) (~52%). The effect of the oxidation of copper(I/II) was examined using copper(I) iodide and copper(II) sulphate (Entries 4 and 5), and the results show that the CuI supported on naturally occurring chitin achieves significant yields compared with $CuSO_4$-chitin in water. Interestingly, the catalyst loading could be further reduced to 1 mol%, leading to a significant yield of 1,4-disubstituted-1,2,3-triazole (84%) within 12 h (Entry 7, Table 1).

After optimising the reaction conditions, several azide and alkyne derivatives were catalysed using the CuI-chitin catalyst (Table 2). The results indicate that CuI-CHT can effectively catalyse the regioselective synthesis of 1,4-disubstituted-1,2,3-triazole derivatives in a click manner. The electron-donating and electron-withdrawing substituents do not have a significant impact on yields or regioselectivity. However, the alkyl-substituted azide shows a moderate yield (Entry 15). Furthermore, in most cases, the reactions were completed within 12 h, and the corresponding 1,2,3-triazoles did not require any further purification.

The catalytic activity of CuI-CHT was also tested in three components [3 + 2] cycloaddition reactions of terminal alkynes, sodium azides and alkyl halides (see Scheme 2). The results show that the 1,4-triazole product was formed under a regioselective manner with high yield at room temperature by using catalyst copper loadings of 2 mol% (Table 3). A higher copper loading did not promote this click reaction whereas a lower amount of catalyst conducts to a lower yield of 1,4-disubstituted-1,2,3-triazoles. Further, the reaction scope of this CuAAC reaction was investigated, and the results show that the desired products can be obtained in excellent yields within 24 h (Table 4). The substituted benzyl bromides or alkynes had not any great significant effect on the catalytic activity of our catalyst in these reactions. Moreover, the 1,4-regioisomer was the only regioisomer obtained in these reactions.

In order to investigate the applicability of CuI-CHT, a comparative study of the catalyst and other reported catalysts was conducted, the results being compiled in Table 5. The reaction between phenylacetylene (**1a**) and benzyl azide (**2a**) was chosen as the model reaction. The results indicate that CuI-CHT is more efficient than the - Cu(II)-alginate hydrogels, Cu(II)-alginate, Cu(II)-poly (hydroxamic acid), Cu(II)-polyethylenimine and $CuSO_4$-PEG-PS catalysts and also that it is similar, in terms of sustainability and catalytic reactivity, to the Cu(I)-cellulose. However, the prepared catalyst has a lower catalytic activity compared with those of the Cu(I)-AMPS, Cu(II)-hydrotalcite and Cu NPs@hydrotalcite catalysts. Indeed, the highly functionalisation of this polysaccharide makes



SCHEME 1 [3 + 2] Cycloaddition azide–alkyne catalysed by the Cu-CHT catalyst

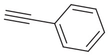
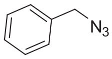
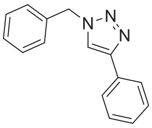
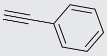
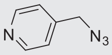
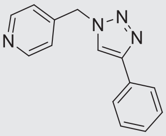
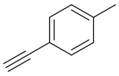
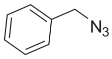
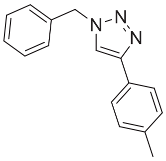
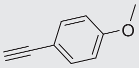
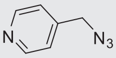
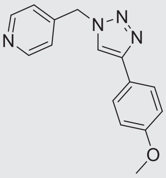
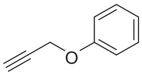
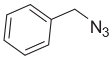
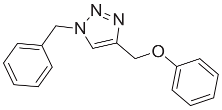
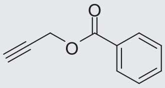
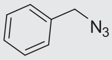
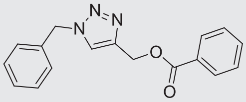
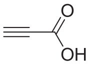
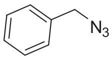
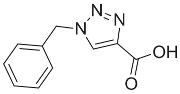
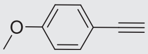
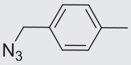
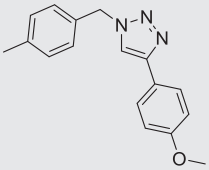
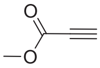
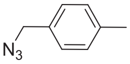
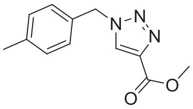
TABLE 1 Optimisation of the reaction conditions for the click reaction catalysed by the Cu-CHT catalyst

Entry	Catalyst	Loading (mol%)	Time (h)	Yield (%)[a]
1	Neat	-	24	0
2	α-Chitin	-	24	0
3	CuI	5	24	52
4	CuI-CHT	5	12	96
5	$CuSO_4$-chitin	5	24	65
6	CuI-CHT	3	12	94
7	CuI-CHT	1	12	90
8	CuI-CHT	0.5	12	75

Note: Conditions: benzyl azide (0.6 mmol), phenyl acetylene (0.5 mmol), solvent (3 cm^3) and catalyst at room temperature.

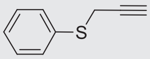
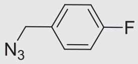
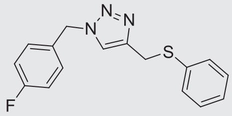
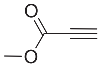
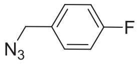
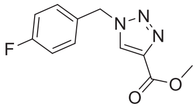
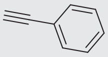
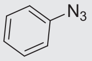
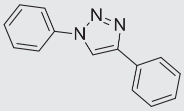
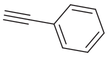
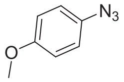
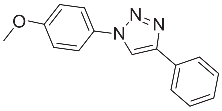
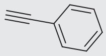
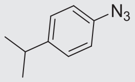
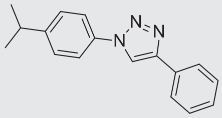
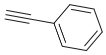
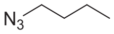
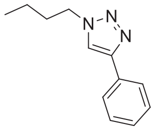
[a] Isolated yields.

TABLE 2 Synthesis of the corresponding 1,2,3-triazoles (**3a–3j**) using the CuI-CHT catalyst

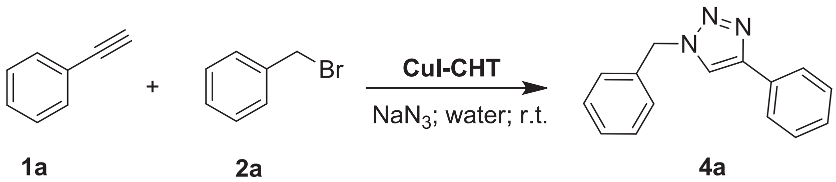
Entry	Alkyne	Azide	Product		Yield[a] (%)
1				**3a**	90
2				**3b**	90
3				**3c**	92
4				**3d**	87
5				**3e**	89
6				**3f**	87
7				**3g**	84
8				**3h**	89
9				**3i**	75

(Continues)

TABLE 2 (Continued)

Entry	Alkyne	Azide	Product		Yield[a] (%)
10				**3j**	86
11				**3k**	79
12				**3l**	86
13				**3m**	89
14				**3n**	92
15				**3o**	52

Note: Reaction conditions: azide (0.6 mmol), alkyne (0.5 mmol), water (3 cm^3) and CuI-CHT (1 mol%) at room temperature (12 h).
[a]Isolated yields.



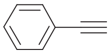
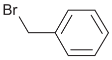
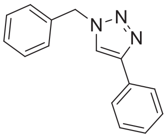
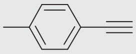
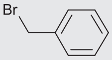
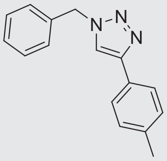
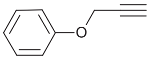
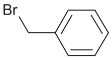
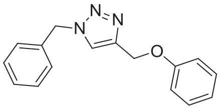
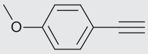
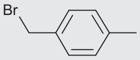
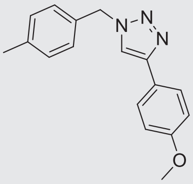
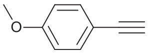
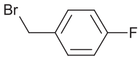
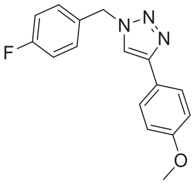
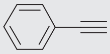
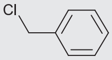
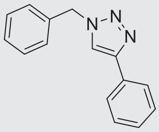
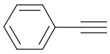
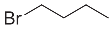
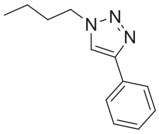
SCHEME 2 One-pot synthesis of 1,4-disubstituted-1,2,3-triazoles catalysed by CuI-CHT

TABLE 3 Optimisation of the reaction conditions for the one-pot CuAAC reaction using the CuI-CHT catalyst

Entry	Catalyst	Loading (mol %)	Time (h)	Yield (%)[a]
1	Neat	-	24	0
2	CuI	5	24	61
3	CuI-CHT	5	24	98
4	CuI-CHT	2	24	96
5	CuI-CHT	2	12	69
5	CuI-CHT	1	24	56

Note: Conditions: benzyl bromide (0.6 mmol), phenyl acetylene (0.5 mmol), H_2O (5 cm^3) and catalyst at room temperature.
[a]Isolated yields.

TABLE 4 One-pot synthesis of 1,4-disubstituted-1,2,3-triazoles using the CuI-CHT catalyst

Entry	Alkyne	Azide	Product		Yield^a (%)
1				**4a**	96
2				**4b**	98
3				**4c**	90
4				**4d**	92
5				**4e**	85
6				**4f**	92
7				**4g**	54

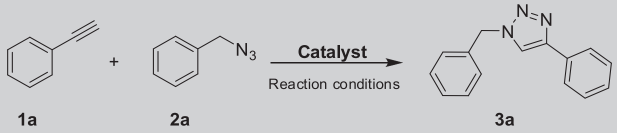
Note: Conditions: alkyl halides (0.6 mmol), alkyne (0.5 mmol), NaN_3 (0.6 mmol), CuI-CHT (2 mol%) and H_2O (5 cm^3) at room temperature (24 h).
^{a}Isolated yield.

it an excellent polymeric skeleton for the immobilisation of copper ions, constituting then a very appealing sustainable catalytic material. The undemanding preparation and reaction mixtures, as well as the lack of reducing agents, make this catalyst easily adaptable and more sustainable.

3.3 | Mechanistic study

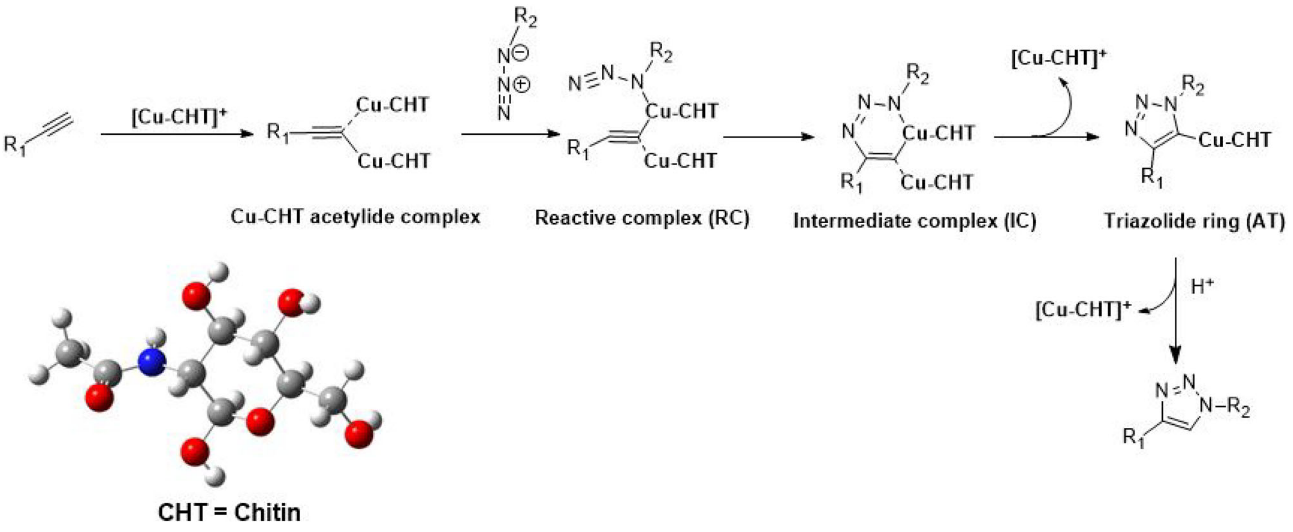
In order to explain the catalytic activity of the proposed catalyst in azide–alkyne cycloaddition reactions and to better understand the reaction mechanism,[36–44] density functional theory (DFT) calculations were conducted at

TABLE 5 A comparison of our protocol with other reported protocols for the click synthesis of 1,4-disubstituted-1,2,3-triazole derivatives



Entry	Catalyst	[Cu] Loading (mol%)	Conditions	Time (h)	Yield (%)	Ref.
1	CuI-CHT	1	H_2O, r.t.	12	90	This work
2	Cu(II)-alginate hydrogel	2	H_2O, r.t.	48	93	Bahsis et al.[20]
3	Cu(II)-alginate	21	H_2O, r.t.	18	98	Goodrich, and Winter[32]
4	Cu(II)-cellulose	1.2	H_2O, r.t.	12	96	Bahsis et al.[17]
5	Cu(I)-cellulose	0.14	H_2O, r.t.	4	93	
6	Cu(II)-poly (hydroxamic acid)	0.1	H_2O, 50°C	4	91	Reddy et al.[33]
7	Cu(II)-polyethylenimine	5	H_2O, r.t.	24	98	Mandal et al.[34]
8	$CuSO_4$-PEG-PS	5	H_2O, N_2, r.t., sodium ascorbate (10 mol%)	12	97	El Ayouchia et al.[35]
9	CS-Fe_3O_4-Cu(II)	1.54	CH_2Cl_2, r.t.	12	78–89	Chetia et al.[36]
10	Cu NPs@hydrotalcite	10[a]	C_2H_3N, r.t.	6–12	75–89	Namitharan et al.[37]
11	Cu(I)-AMPS	1	Water, r.t.	1–2	80–98	Bahsis et al.[18]

Abbreviations: AMPS, aminomethyl polystyrene; CS, chitosan; PEG-PS, poly(ethylene glycol)-polystyrene.
[a] In milligrams.



SCHEME 3 Proposed mechanism of the CuAAC catalysed by Cu(I)-CHT

the M062X/6-31G(d,p) (LANL2DZ for Cu) level using water as a solvent in the CPCM model. As illustrated in Scheme 3, the model complex of the CuI-chitin catalyst was chosen as the appropriate model for the CuI-CHT with benzyl azide and phenyl acetylene as the starting materials for the CuAAC reaction. In fact, the reaction between the copper(I)-chitin complex and the terminal alkyne contributes to the formation of the copper-acetylide complex (Scheme 3).[39–47] This interaction leads to the formation of the reactive complex (RC) intermediate. This step is highly exothermic in water with 4.24 kcal mol^{-1} (Figure S1). These interactions lead to the formation of a six-membered copper-containing intermediate complex (IC). Furthermore, a reductive elimination step leads to the formation of the triazolide ring (AT) (Scheme 3).[48–50] Finally, the protonation of the triazolide complex results into the formation of the corresponding 1,4-disubstituted-1,2,3-triazole, which is in good agreement with the experimentally observed regioselectivity.[51,52]

3.4 | Reusability of the catalyst

The reusability of the CuI-CHT catalyst for the AAC reaction of phenylacetylene (**1a**) and benzyl azide (**2a**) in water at room temperature using optimised reaction conditions was also investigated (Scheme 3). After 12 h, the reaction mixture was diluted with dichloromethane, and the catalyst was recovered through simple filtration. It was then washed, dried and used for the next run. Importantly, the catalytic activity and selectivity of the catalyst did not significantly decrease for the next four consecutive runs (Table 6). The structure of the recovered catalyst was analysed by conducting a SEM and an EDX analysis (Figures 7 and 8). The SEM analysis shows a smaller surface morphology in both fresh and recycled catalysts, whereas the EDX data used in the ICP analysis show a decrease in the copper percentage of the catalyst after four runs ([Cu] = 4.89%). Moreover, a very low copper concentration in the final 1,2,3-triazolic products was revealed by ICP analysis (less than 1 ppm). The simple structure, catalytic activity and recyclability of the CuI-CHT catalyst make it more environmentally benign.

TABLE 6 Recycling of the CuI-CHT catalyst in the CuAAC reaction

Run	Yield[a] (%)
1	82
2	79
3	72
4	68

[a] Isolated yield after 12 h.

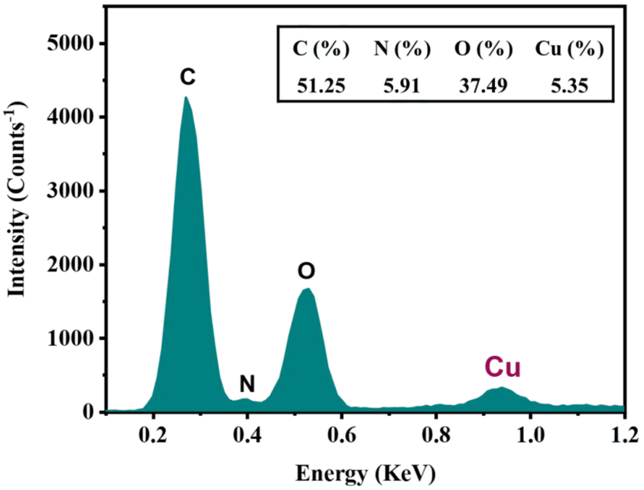


FIGURE 8 Energy-dispersive X-ray (EDX) spectrum of the CuI-CHT recycled catalyst

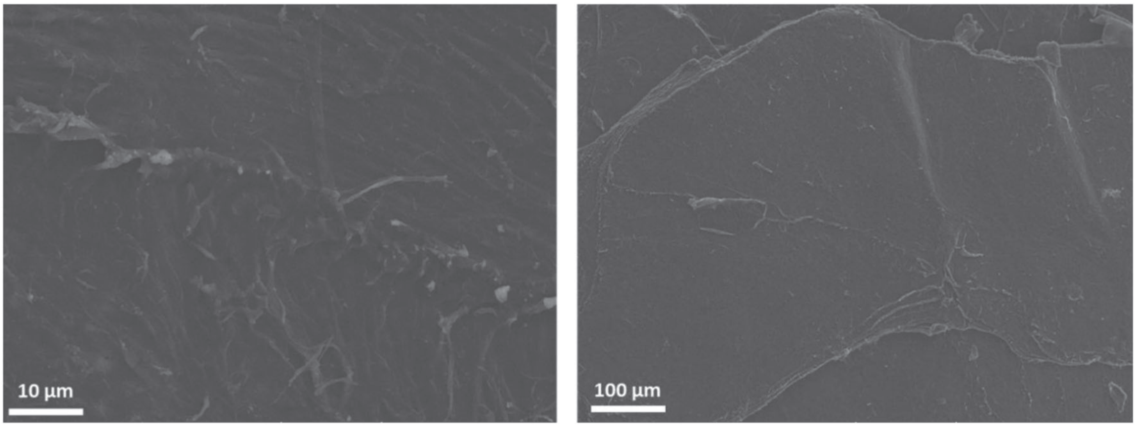


FIGURE 7 Scanning electron microscopy (SEM) analysis of the CuI-CHT recycled catalyst

4 | CONCLUSION

This work reports the development of a new environmentally friendly polysaccharide α-chitin-supported copper(I) ion (CuI-CHT) as a new heterogeneous catalyst for the CuAAC reactions. The proposed catalyst was successfully synthesised through the coordination of copper(I) with the naturally occurring chitin polymer and characterised by FT-IR, SEM, EDX, XRD, TGA and AAS. The CuI-CHT catalyst shows high catalytic activity for the regioisomer synthesis of 1,4-disubstituted-1,2,3-triazoles using water as solvent and working at room temperature. The reusability study shows that the catalyst can be reused until four cycles in CuAAC reactions under greener conditions, illustrating the sustainability of the present protocol. Furthermore, DFT calculations were used to account for the regioselectivity outcome of the Cu(I)-chitin catalyst in the CuAAC reaction.

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AUTHOR CONTRIBUTIONS

Lahoucine Bahsis: Conceptualization; data curation. **El-Houssaine Ablouh:** Data curation; formal analysis; methodology. **Mouhi Eddine Hachim:** Methodology; software. **Hafid Anane:** Methodology; software; validation. **Moha Taourirte:** Resources. **Miguel Julve:** Formal analysis; resources. **Salah-Eddine Stiriba:** Conceptualization; formal analysis; validation.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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