Bio-waste corn-cob cellulose supported poly(hydroxamic acid) copper complex for Huisgen reaction: Waste to wealth approach

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ABSTRACT

Corn-cob cellulose supported poly(hydroxamic acid) Cu(II) complex was prepared by the surface modification of waste corn-cob cellulose through graft copolymerization and subsequent hydroximation. The complex was characterized by IR, UV, FESEM, TEM, XPS, EDX and ICP-AES analyses. The complex has been found to be an efficient catalyst for 1,3-dipolar Huisgen cycloaddition (CuAAC) of aryl/alkyl azides with a variety of alkynes as well as one-pot three-components reaction in the presence of sodium ascorbate to give the corresponding cycloaddition products in up to 96% yield and high turn over number (TON 18,600) and turn over frequency (TOF 930 h^{-1}) were achieved. The complex was easy to recover from the reaction mixture and reused six times without significant loss of its catalytic activity.

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1. Introduction

The Cu(I) catalyzed Huisgen 1,3-dipolar cycloaddition of azide-alkyne, the most common "Click" reaction discovered by Sharpless and co-workers (Huisgen, 1963; Rostovtsev, Green, Fokin, & Sharpless, 2002; Tornoe, Christensen, & Meldal, 2002) have stimulated an increasing interest for a wide range of pharmaceuticals and medicinal chemistry such as anti-bacterial, anti-viral, antibiotic, magnetic resonance imaging, anti-allergic and trypanocidal activities (Goh, Chai, & Chen, 2014; Hassan & Müller, 2015; Jiang et al., 2015; Koganei, Tachikawa, E-Zaria, & Nakamura, 2015; Lee et al., 2007; Papadopoulou et al., 2012; Silva et al., 2008; Tang & Becker, 2014; Thomas, Adhikari, & Shetty, 2010; Wacharasindhu, Bardhan, Wan, Tabei, & Mansour, 2009; Xia et al., 2006). The early Huisgen cycloaddition process required a strong electron-withdrawing substituent on either azide or alkyne, high temperature, long reaction time and it often afforded a mixture of 1,4-and 1,5-disubstituted isomers (Tornoe et al., 2002). So far, Cu(I) salts, Cu(II) salts together with a reducing agent (Tavassoli et al., 2015), Cu(II)/Cu(0) comproportionation (Appukkuttan, Dehaen, Fokin, & der Eycken, 2004), mixed Cu/Cu-oxide nanoparticles (Pachón, Maarseveen, & Rothenberg, 2005), CuSO₄/sodium ascorbate (Bock, Hiemstra, & Maarseveen van, 2006; Kim, Park, Kang, Song, & Park, 2010), CuI/PEG-400, (Daugaard, Hvilsted, Hansen, & Larsen, 2008) and Cu(OAc)₂·3H₂O/H₂O (Rajender, Uma, Rajgopal, & Lakshmi, 2008) have been used as catalysts for the Huisgen cycloaddition reaction. Recently, Cu(II) catalyzed Huisgen reaction have been reported and their mechanism also described (Brotherton et al., 2009; Jiang et al., 2014; Kantam, Reddy, & Rajgopal, 2006; Kuang, Michaels, Simmons, Clark, & Zhu, 2010;). However, these homogeneous catalyzed Huisgen reactions have major disadvantages associated with the difficulties in recovery of metal catalysts and reuse for successive reaction cycles as well as the possibility of metal contamination in the end-products. In order to overcome these drawbacks, recent works have concentrated on heterogeneous catalytic systems which have several advantages like good dispersion of active sites, easier and safer handling, easy separation of the products from the reaction mixture and reusability of the catalyst. Thus, a good number of heterogeneous catalytic systems have been developed. For instance, copper on charcoal (Lipshutz & Taft, 2006), zeolites (Chassaing, Kumarraja, Sido, Pale, & Sommer, 2007), polymers (Gala et al., 2014; Girard et al., 2006; Tano, Mieda, Sugimoto, Ogura, & Itoh, 2014; Tavassoli et al., 2015; Yamada, Sarkar, & Uozumi, 2012), non-magnetic and magnetic supported variants (Fernandez, Munoz, Jaramillo, Mateo, & Gonzalez, 2010), hydroxyapatite (Masuyama, Yoshikawa, Suzuki, Hara, & Fukuoka, 2011), silica (Mnasri et al., 2015; Roy et al., 2014) and dendrimer nanoreactor (Deraedt, Pinaud, & Astruc, 2010) have been reported.

However, long reaction times, high temperature, formation of homocoupling products of alkynes (Glaser coupling) and the use of large amounts of copper catalysts are the drawbacks of these methods (Eglinton & Galbraith, 1956; Siemsen, Livingston, & Diederich, 2000). Therefore, the development of a reusable, eco-friendly and more convenient catalyst for the regioselective synthesis of 1, 4-disubstituted 1,2,3-triazoles still remains a major challenge.

In the recent years, scientists are searching for more nature-friendly as well as sustainable resources and processes. Thus, biopolymers like alginate, gelatin, starch, and chitosan derivatives have been utilized as supports for catalytic applications (Huang, Xue, Hu, Huang, & Jiang, 2002; Wei, Zhu, Zhao, Huang, & Jiang, 2004; Zhang et al., 2001). Cellulose, a biopolymer can also be a very suitable candidate for this purpose because of its low-cost, wide natural abundance, ubiquitous availability and bio-renewable character. In view of these advantages, natural cellulose have been considered as a highly desirable alternative substance as a solid support of metal catalysts (Guibal, 2005; Reddy, Kumar, Sreedhar, & Kantam, 2006). Furthermore, chemical modifications of primary or secondary hydroxyl groups in cellulose allow introducing an effective chelating ligands on to the cellulose backbone (Islam et al., 2016; O'Connell, Birkinshaw, & O'Dwyer, 2008).

Corn-cob is left as waste but it is a potential source of cellulose. If it could be used intelligently, this waste may come out as wealth instead of waste. In this context, we have recently developed waste corn-cob cellulose supported poly(amidoxime) ligand which had been successfully applied for the removal of metal ions from wastewater and the anchored metal (Cu) in this ligand has been used as an efficient catalyst for Aza-Michael reactions (Islam et al., 2016; Rahman, Rohani, Mustapa, & Yusoff, 2014; Rahman et al., 2016a, 2016b, 2016c; Sarkar, Sultana, Biswas, Rahman, & Yusoff, 2016). As a continuation of our studies, herein we report waste corn-cob cellulose supported poly(hydroxamic acid) Cu(II) complex catalyzed Huisgen 1,3-dipolar cycloaddition reaction in the presence of sodium ascorbate under mild reaction conditions.

2. Experimental

2.1. Graft copolymerization

Pure cellulose was extracted from waste corn-cob according to the method described elsewhere (Rahman et al., 2014, 2016a). Graft copolymerization reaction was carried out in 1 L three-neck round bottom flask equipped with stirrer and condenser in thermostat water bath. The cellulose slurry was prepared by stirring 4.0 g of corn-cob in 400 mL distilled water for overnight. The mixture was then heated to 55 °C with stirring and 1.1 mL of diluted sulphuric acid (50%) was added. After being stirred for 5 min, 1.10 g of ceric ammonium nitrate (CAN, 10 mL aqueous solution) was added and the reaction mixture was stirred under nitrogen atmosphere. After 20 min, 10 mL methyl acrylate purified monomer was added into the reaction flask and stirred for another 4 h under nitrogen atmosphere. The mixture was cooled, filtrated on a glass filter and washed several times with aqueous methanol (methanol: water: 4:1) to give corn-cob cellulose supported poly(methyl acrylate) 1. The product was finally oven dried at 50 °C to get a constant weight and yield of grafted copolymer was 8.48 g Rahman et al., 2016a, 2016b, 2016c.

2.2. Synthesis of poly(hydroxamic acid) ligand 2

Hydroxylamine solution was prepared by dissolving 10 g of hydroxylamine hydrochloride (NH$_2$OH·HCl) in 300 mL of aqueous methanol (methanol: water; 4:1). A cold NaOH solution (50%) was added into the hydroxylamine solution when NaCl was precipi-

tated out and it was removed by filtration. The pH of the reaction mixture was adjusted to 11 by controlled addition of NaOH solution and the ratio of methanol and water was maintained at 4: 1 (v/v). The poly(methyl acrylate) grafted corn-cob cellulose 1 (4.5 g) was placed into a two-neck round bottom flask equipped with a stirrer, condenser and thermostat water bath. The prepared hydroxylamine solution was then added to the flask and the reaction was carried out at 70 °C for 6 h. The resulting chelating polymeric ligand 2 was separated from hydroxylamine solution by filtration followed by washing with aqueous methanol. Further, the ligand 2 was treated with 200 mL of 0.1 M HCl (in methanol) solution for 5 min to neutralize the reaction mixture. The ligand was filtered and washed several times with methanol and dried at 50 °C to obtain a constant weight (Rahman et al., 2016a, 2016b, 2016c).

2.3. Preparation of the poly(hydroxamic acid) Cu(II) complex 3

An aqueous solution of CuSO$_4$·5H$_2$O (246 mg, in 10 mL H$_2$O) was added into a stirred mixture of poly(hydroxamic acid) ligand 2 (1 g) in 25 mL water at room temperature. The blue CuSO$_4$ was immediately turned into green colour and the mixture was stirred for 2 h at room temperature. The reaction mixture was filtrated and washed several times with NH$_4$Cl, water, MeOH and dried at 60 °C for 1 h (1.033 g). The ICP-AES analysis showed that 0.5 mmol/g of copper (Sarkar et al., 2016) was coordinated with the poly(hydroxamic acid) ligand.

2.4. General procedure for the one-pot three-component Huisgen reaction

A 5-mL glass vessel was charged with 3 (1 mg, 0.05 mol%), alkyne (1 mmol), sodium azide (1.1 mmol), and the corresponding aryl halide (1 mmol) in 3 mL 5 mol% aqueous solution of sodium ascorbate. The reaction mixture was stirred at 70 °C for 3 h during which time colourless triazoles were precipitated. The reaction mixture was diluted with EtOAc and the insoluble 3 was recovered by centrifugation. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 2 mL). The combined organic layers were dried over MgSO$_4$, and concentrated under reduced pressure to give the corresponding 1,2,3-triazole. The crude product was purified by silica gel column chromatography (EtOAc/hexane, 1:4).

2.5. General procedure for Huisgen reaction of azides and terminal alkynes

The aromatic/aliphatic azide (1 mmol), alkyne (1 mmol), copper complex 3 (0.05 mol%) and sodium ascorbate 5 mol% (3 mL) were measured in a 5 mL glass vessel and the reaction mixture was heated at 70 °C for 2.5 h. After completion of the reaction, it was cooled to room temperature and diluted with ethyl acetate. The copper complex 3 was removed by centrifugation and the organic layer was extracted with ethyl acetate, dried over MgSO$_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc/hexane, 1:4) to give the corresponding triazole.

2.6. Recycling of the Cu(II) complex 3

The recycle experiment was done for the reaction of phenylacetylene (4a), benzyl azide (5a) in the presence of sodium ascorbate (Table 1) using 0.25 mol% (5 mg) of 3 at 70 °C. The Cu(II) complex 3 was recovered and reused by the following steps: after competition of the first cycle, the reaction mixture was cooled to room temperature, diluted with EtOAc and centrifuged. The organic and aqueous layers were decanted and the remained solid catalyst (in the glass vessel) was washed by water, methanol and dried at

Table 1
Optimization of the Huisgen reaction.[a]

Ph—≡ + N₃⌒Ph →[**3** / sodium ascorbate (5 mol%, 3 mL)] → 6a product

Entry	**3** (mol%)	Temp. (°C)	Time (h)	Yield (%)
1	0.1	50	4	91
2	0.5	70	3.5	96
3	0.05	50	5	94
4	0.05	70	2.5	96
5	0.005	70	6	91
6	0.005	80	5	94
7	0.005	90	2.5	94
8[b]	–	70	2.5	0
9[c]	**2** (0.05)	70	2.5	10

[a] Conditions: **4** (1 mmol), **5** (1 mmol), **3** (0.1–0.005 mol%), sodium ascorbate (5 mol%, 3 mL).
[b] Reaction was carried out without **3**.
[c] Reaction was carried out using **2**.

Fig. 1. IR spectrum of (a) corn-cob cellulose, (b) poly(methyl acrylate) **1**, (c) poly(hydroxamic acid) **2**, (d) Cu(II) complex **3**.

80 °C under vacuum. The reaction glass vessel was then charged with phenylacetylene (**4a**), benzyl azide (**5a**), sodium ascrobate and the reaction was carried out without changing the reaction conditions (Fig. 3a).

3. Results and discussion

The waste corn-cobs were successively boiled with NaOH and glacial acetic acid. The resulting cellulose was washed with water and bleached with hydrogen peroxide to obtain pure cellulose (Rahman et al., 2014, 2016a). The cellulose supported poly(methyl acrylate) **1** was obtained by the graft copolymerization of cellulose with methyl acrylate in the presence of CAN as an initiator under the nitro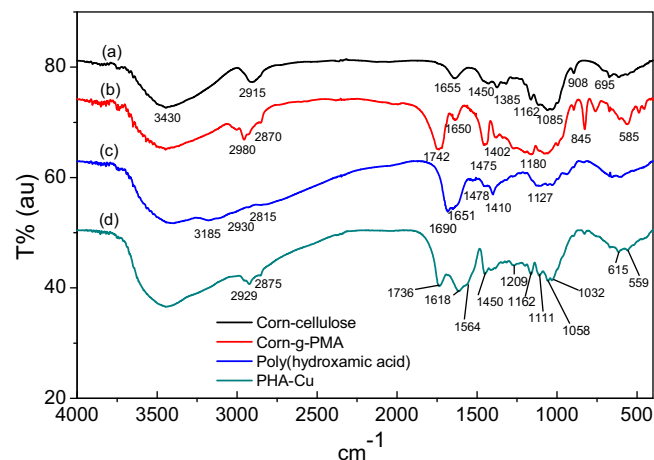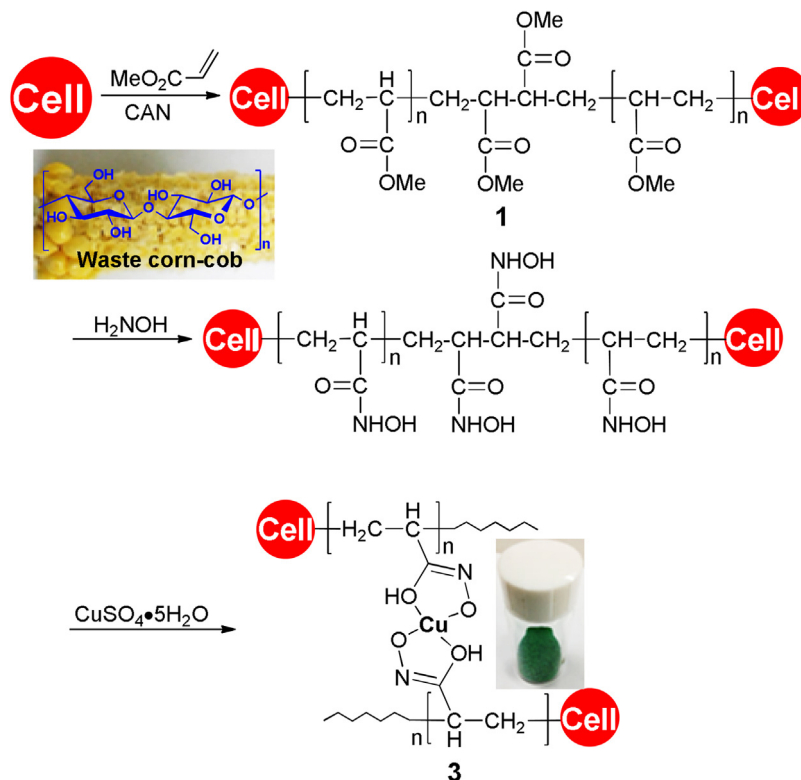gen atmosphere and product **1** was obtained about 112% grafted copolymer. The poly(methyl acrylate) **1** was treated with hydroxylamine to produce poly(hydroxamic acid) chelating ligand **2** with 98% conversion (Rahman et al., 2014), which was further treated with aqueous CuSO₄ to give green colour cellulose supported Cu(II) complex **3** (Cu, 0.5 mmol/g, ICP-AES) (Scheme 1).

The IR spectrum of fresh corn-cob cellulose showed adsorption bands at 3430 and 2915 cm⁻¹ which referred to O—H and C—H stretching, respectively (Fig. 1). The band at 1655 cm⁻¹ was due to the bending mode of OH (Bonacorso et al., 2013) and a smaller peak at 1450 cm⁻¹ was observed for CH₂ symmetric stretching. The absorbance at 1385 and 1162 cm⁻¹ originated from the O—H bending and C—O stretching, respectively. The C—O—C pyranose ring skeletal vibration was observed at 1085 cm⁻¹. A small sharp peak at 908 cm⁻¹ corresponded to the glycosidic C_1—H deforma-

Scheme 1. Synthesis of cellulose supported Cu(II) complex **3**.

tion with ring vibration contribution and OH bending indicating β-glycosidic linkages between glucose units in cellulose (Chuan et al., 2006). The IR spectrum of poly(methyl acrylate) grafted cellulose **1** showed new absorption band at 1475 and 1402 cm^{-1} due to scissoring and wagging stretching of the methyl group respectively (Haron, Tiansih, Ibrahim, Kassim, & Wan Yunus, 2009). In addition, new absorption bands at 1742 and 845 cm^{-1} due to C=O and CH$_3$ stretching (Rahman et al., 2016b) were found. Whereas, the peaks at 2980 and 2870 cm^{-1} represent C—H (sp^3) stretching of the methyl group. The poly(hydroxamic acid) **2** showed new absorption bands at 1690 and 1651 cm^{-1} corresponding to the C=O stretching and N—H bending modes. Additionally, a new broad band at 3185 cm^{-1} for N—H stretching and 1410 cm^{-1} for OH bending were observed. It was found that the C=O band at 1742 cm^{-1} in **1** shifted to lower wavelength 1690 cm^{-1} which confirmed the successful production of hydroxamic acid ligand onto the corn-cob cellulose. After incorporation of copper salt with the poly(hydroxamic acid) ligand, the colour of **2** changed to green colour and a new absorption band at 1736 cm^{-1} was observed which corresponding to C=O stretching for hydroxamic acid (Prenesti & Berto, 2002; Rafiee-Moghaddam et al., 2014). The peaks are at 1618, 1209 and 1162 cm^{-1} were assigned for C=N and C—O stretching respectively. A peak at 615 cm^{-1} confirmed the successful incorporation of Cu(II) with the poly(hydroxamic acid) ligand **2** (Rafiee-Moghaddam et al., 2014).

The FESEM of corn-cob cellulose showed wooden stick like morphology (Fig. 2a) whereas, poly(methyl acrylate) **1** grafted cellulose showed distinguishable grafting occurred on the surface of wooden stick like cellulosic structure having rough surface surrounding the stick (Fig. 2b). The poly(hydroxamic acid) chelating ligand **2** showed small spherical shaped morphology (Fig. 2c) whereas, poly(hydroxamic acid) ligand after adsorption of Cu(II) showed compact bigger spherical shape morphology (Fig. 2d) which has significantly different characteristics than other surface structures.

The TEM analysis of **3** also displayed the presence of copper (Ø = 17.2 ± 4 nm) onto the cellulose backbone (Fig. 2e). The UV–vis spectrum of **3** exhibited a single absorption at 687 nm (Fig. 2f) which was assigned as Cu-O coordination (Gala et al., 2014; Tano et al., 2014). The EDX spectra (Fig. 2g) also revealed the incorporation of Cu(II) onto the cellulose surface. Furthermore, XPS of Cu 2p$_{3/2}$ showed a peak at 934.5 eV (Fig. 2h) which was assigned for the binding energy of Cu(II) (Yamada et al., 2012). These results suggested that the poly(hydroxamic acid) ligand **2** coordinated with copper to yield corn-cob cellulose supported polymeric Cu(II) complex **3**.

The corn-cob cellulose supported poly(hydroxamic acid) Cu(II) complex 3 was used as the catalyst for the catalytic investigation of Huisgen reaction of organic azides and terminal alkynes. The summary of optimization tests for the cycloaddition of phenylacetylene (**4a**) and benzyl azide (**5a**) to produce 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (**6a**) is depicted in Table 1. Initially, the reaction was carried out using 0.1 mol% of 3 at 50 °C for 4 h in presence of 5 mol% aqueous solution of sodium ascorbate and the reaction was smoothly afforded to the desired product 6a in 91% yield (entry 1). Whereas, 96% yield was obtained when the same reaction was performed at 70 °C for 3.5 h (entry 2). We observed that, reaction time is periodically increased upon decreasing the catalyst loading, (entries 3–5) and reaction time is decreased when the temperature is increased (entries 6 & 7). It is noted that sodium ascorbate reduced Cu(II) to Cu(I), by changing the colour of Cu(II) complex 3 from green to yellow during the reaction. The cycloaddtion reaction was not proceeded at all when the reaction was carried out without copper complex 3 (entry 8). However, only 10% yield was obtained when poly(hydroxamic) acid was used (entry 9). Hence, from the screening of the reaction progress it can be concluded that catalytic loading 0.05 mol% and reaction temperature 70 °C would be

the suitable condition (entry 4) to carry out the Huisgen reaction with this Cu(II) complex **3**.

Having the optimum reaction conditions in hand, we applied the Cu(II) complex **3** to a variety of azides and alkynes. The *p*-methyl/methoxy substituted benzyl azides (**5b**) and (**5c**) efficiently reacted with **4a** under optimized reaction conditions to afford the corresponding triazoles **6b** and **6c** in up to 95% yield (Table 2, entries 1 & 2). The substituted alkyne i.e. *p*-tolylacetylene (**4b**) reacted with benzyl azide (**5a**), 1-azido-2-phenylethane (**5d**) and 1-azidodecane (**5e**) to generate the corresponding products **6d-f** in 91–96% yields (entries 3–5). An aliphatic alkynol, hex-5-yn-1-ol (**4c**) readily reacted with a variety of benzylic and aliphatic azides to give the corresponding triazoles **6g-k** in 89–96% yields (entries 6–10). The Cu(II) complex **3** also promoted the reaction of alkynes bearing tertiary alcohol, acetal, and amine moieties with **5a** to give the corresponding products **6l-n** in 90–92% yields (entries 11–13). It is interesting to note that alcohol, acetal and amine groups remained intact and they did not affect the reactivity of **3** during the cyclization. Therefore, **3** is tolerant to different functional groups/functionalities in both alkynes and azides.

The recycling of the catalyst plays an important role in heterogeneous catalytic system. So, our attention turned to the reusability of **3**. After completion of the reaction of **4a** with **5a**, the complex **3**, recovered by centrifugation was washed with water, methanol and dried at 80 °C. It was then used in the next run under identical reaction conditions. Following this process, the complex **3** was submitted to the reactivity process for six successive turns under the same conditions (Fig. 3a). Only slight loss of catalytic activity was observed for initial run was due to the loss of **3** during the centrifugation process. No copper species was leached out into the reaction mixture (ICP-AES) from the support during the reaction progress. Thus, it is reasonable to believe that the cellulose supported poly(hydroxamic acid) Cu(II) complex **3** has high stability and can be repeatedly used without significant loss of its catalytic activity.

A hot filtration test was also conducted to justify the heterogeneity of the cellulose supported Cu(II) complex **3** during cycloaddition reactions. The experiment was performed in a similar manner as the Huisgen cycloaddition reaction (Table 1, **6a**). After 52% conversion (1 h), the reaction mixture was filtered off at hot conditions, and the aqueous solution was heated under identical reaction conditions for an additional 3 h as well as was analyzed for further conversions (Fig. 3b). No more starting material was converted to

Table 2
Huisgen cycloaddition reaction of azides and alkynes.[a]

$$R^1{\equiv} + N_3{\diagup}R^2 \xrightarrow[\substack{\text{sodium ascorbate (5 mol\%)} \\ 70\,°C,\ 2.5\,h}]{\textbf{3}\ (0.05\ \text{mol\%})} \underset{\textbf{6}}{\overset{R^1}{N{-}N{-}N{-}R^2}}$$

Entry	R^1	R^2	Yield (%)
1	**4a**	**5b** (*p*-MeC$_6$H$_4$)	**6b** 94
2	**4a**	**5c** (*p*-MeOC$_6$H$_4$)	**6c** 95
3	**4b** (*p*-MeC$_6$H$_4$)	**5a**	**6d** 96
4	**4b**	**5d** (PhCH$_2$)	**6e** 93
5	**4b**	**5e** (*n*-C$_9$H$_{19}$)	**6f** 91
6	**4c** (HO-(CH$_2$)$_4$)	**5b**	**6g** 92
7	**4c**	**5d**	**6h** 90
8	**4c**	**5e**	**6i** 89
9	**4c**	**5f** (*p*-NO$_2$C$_6$H$_4$)	**6j** 96
10	**4c**	**5g** (*o*-napth)	**6k** 94
11	**4d** [*c*-(CH$_2$)$_5$C]OH	**5a**	**6l** 92
12	**4e** ((EtO)$_2$CH)	**5a**	**6m** 91
13	**4f** (NMe$_2$CH$_2$)	**5a**	**6n** 90

[a] Conditions: **4** (1 mmol), **5** (1 mmol), **3** (0.05 mol%), sodium ascorbate (5 mol%, 3 mL), 70 °C, 2.5 h.
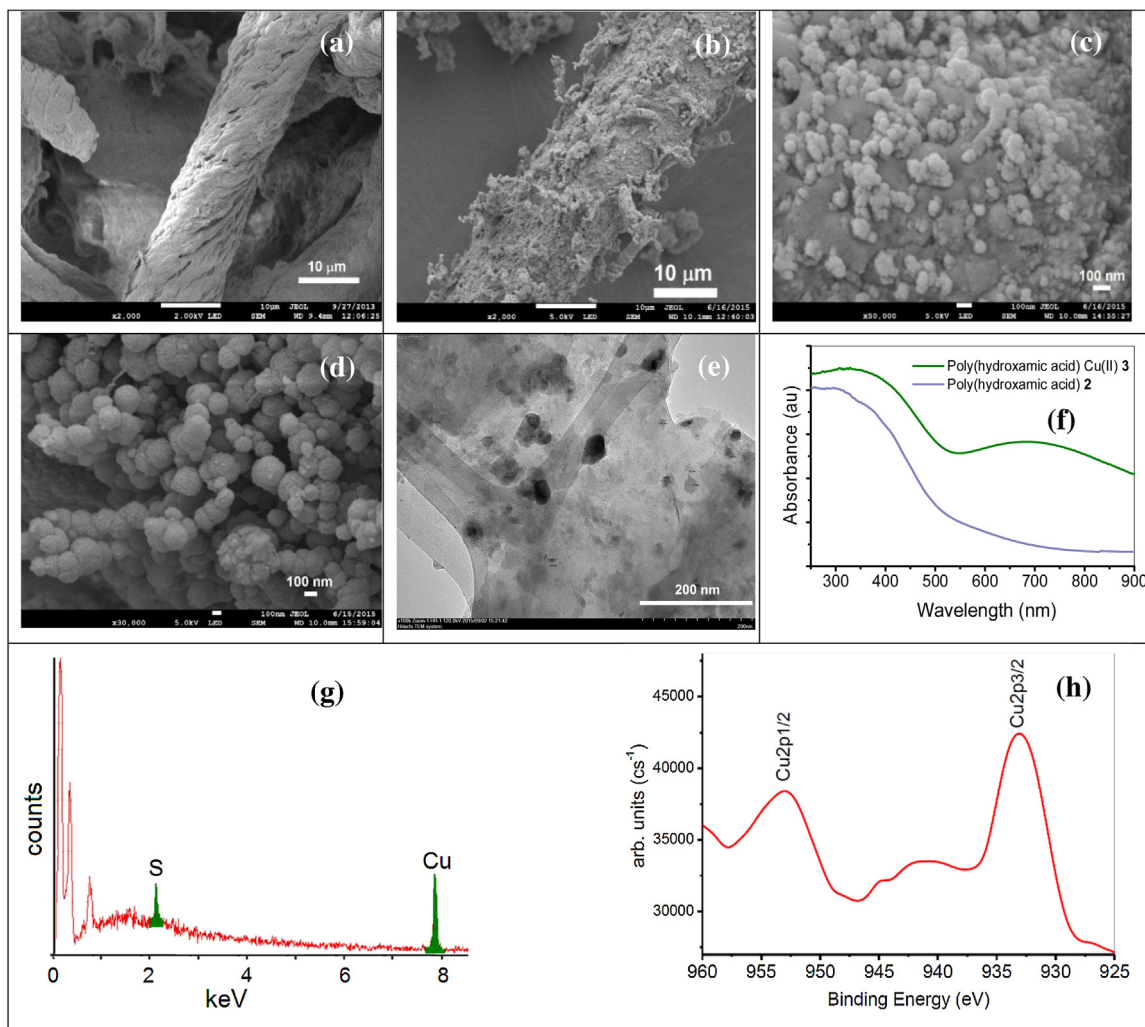
Fig. 2. (a) SEM image of corn-cob cellulose, (b) poly(methyl acrylate) **1**, (c) poly(hydroxamic acid) **2**, (d) Cu(II) complex **3**, (e) TEM of **3**, (f) UV–vis spectrum of **2** & **3**, (g) EDX of **3**, (h) XPS of **3**.

the corresponding product after removal of the Cu(II) complex **3** from the reaction mixture (Phan, Sluys, & Jones, 2006). This experiment indicated that the Huisgen reactions proceeded through the heterogeneous catalytic pathway.

Since **3** efficiently drove the click reaction of alkynes and organic azides, the one-pot three-component cyclization of aryl/alkyl halides, sodium azide and alkynes were also investigated (Table 3). The reaction of phenylacetylene (**4a**), benzyl bromide (**7a**) and

sodium azide was carried out in presence of 5 mol% sodium ascorbate at 70 °C to produce triazole **6a** in 95% yield within 3 h (entry 1). Benzyl chloride (**7b**) was also took part the cycloaddition reaction to give **6a** in 93% yield (entry 2). Benzyl bromide with methyl substituent (**7c**), 2-naphthylmethyl bromide (**7d**), ethyl bromoacetate (**7e**) and cinnamyl chloride (**7f**) efficiently reacted with phenylacetylene (**4a**) to afford the corresponding triazoles **6b**, **6o-q** in 91–95% yields (entries 3–6). The reactions of 4-tolylacetylene (**4b**)
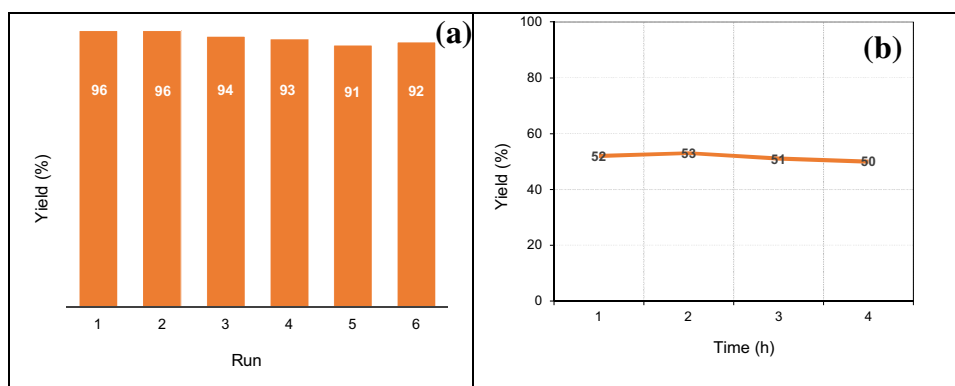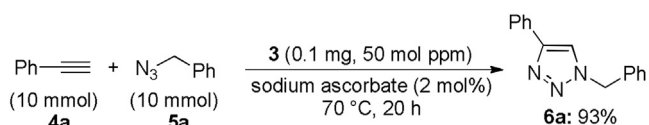

Fig. 3. (a) Huisgen reaction by recycled Cu(II) complex **3**, (b) hot filtration test of Huisgen reaction.
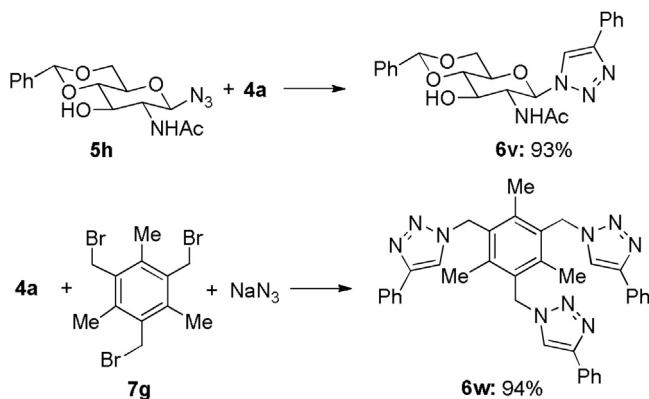
Table 3
Three components Huisgen cycloaddition reaction.[a]

Entry	R[1]	R[2]	Yield (%)
1	**4a**	**7a** (Ph, X = Br)	**6a** 95
2	**4a**	**7b** (Ph, X = Cl)	**6a** 93
3	**4a**	**7c** (p-MeC$_6$H$_4$, X = Br)	**6b** 93
4	**4a**	**7d** (o-naph, X = Br)	**6o** 93
5	**4a**	**7e** (CO$_2$Et, X = Br)	**6p** 95
6	**4a**	**7f** (cinnamyl chloride)	**6q** 91
8	**4b**	**7e**	**6r** 93
9	**4b**	**7c**	**6s** 95
10	**4b**	**7d**	**6t** 94
11	**4c**	**7a**	**6u** 94

[a] Conditions: **4** (1 mmol), **7** (1 mmol), NaN$_3$ (1.1 mmol), **3** (0.05 mol%), sodium ascorbate (5 mol%, 3 mL), 70 °C, 3 h.

TON: 18600; TOF: 930 h^{-1}

Scheme 2. Lower catalytic loadings in the Huisgen reaction.

Scheme 3. Synthesis of functional materials.

and aliphatic alkynes, *i.e.*, hex-5-yn-1-ol (**4c**) with a variety of halides **7a**, **7c**, **7d** and **7e** proceeded smoothly under similar conditions to give the corresponding triazoles **6r-u** in 93–95% yields (entries 8–11). These results indicate that the Cu(II) complex **3** can be readily applied to the combinatorial synthesis of triazole compounds.

To investigate the highest catalytic activity of Cu(II) complex **3** obtainable for cycloaddition, we also performed the Huisgen reaction using 10 mmol of phenylacetylene (**4a**) and benzyl azide (**5a**) in the presence of 50 mol ppm (0.1 mg, 0.005 mol%) of **3**, which still efficiently promoted the cycloaddition reaction to give **6a** in 93% yield (Scheme 2). Turnover number (TON) and turnover frequency (TOF) of the complex reached to 18600 and 930 h^{-1} respectively.

The cellulose supported Cu(II) complex **3** was then used to prepare functional materials (Scheme 3). Reaction of an *N*-acetylglucosamine **5 h** derivative bearing an azide moiety with phenylacetylene (**4a**) was done with **3** under similar reaction conditions, previously described afforded triazole-linked *N*-acetylglucosamine **6 v** in 93% yield. The multi cyclization of **7 g**

with **4a** and sodium azide led to the formation of a tris(triazole) **6 w** in 94% yield.

4. Conclusion

In summary, we prepared highly active bio-waste corn-cob cellulose supported poly(hydroxamic) copper complex which efficiently promoted Huisgen reactions of terminal alkynes and organic azides as well as one-pot three-component cycloadditions. Since we have used waste materials as source of catalytic support and the synthesized catalyst is recyclable, it would be a promising environment-friendly as well as cost-effective bio-heterogeneous catalyst in chemical synthesis. Therefore, waste materials like corn-cob can be utilized as a heterogeneous solid support for metal catalyzed chemical transformation reactions to ensure maximum use of our limited wealth.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2016.09.021.

References

Appukkuttan, P., Dehaen, W., Fokin, V. V., & der Eycken, E. V. (2004). *Organic Letters, 6*(23), 4223–4225.
Bock, V. D., Hiemstra, H., & Maarseveen van, J. H. (2006). *European Journal of Organic Chemistry, 1*, 51–68.
Bonacorso, H. G., Moraes, M. C., Wiethan, C. W., Luz, F. M., Meyer, A. R., Zanatta, N., & Martins, M. A. P. (2013). *Journal of Fluorine Chemistry, 156*, 112–119.
Brotherton, W. S., Michaels, H. A., Simmons, J. T., Clark, R. J., Dalal, N. S., & Zhu, L. (2009). *Organic Letters, 11*(21), 4954–4957.
Chassaing, S., Kumarraja, M., Sido, A. S. S., Pale, P., & Sommer, J. (2007). *Organic Letters, 9*(5), 883–886.
Chuan, F. L., Jun, L. R., Feng, X., Jina, J. L., Jin, X. S., & Run, C. S. (2006). *Journal of Agricultural and Food Chemistry, 54*(16), 5742–5748.
Daugaard, A. E., Hvilsted, S., Hansen, T. S., & Larsen, N. B. (2008). *Macromolecules, 41*(12), 4321–4327.
Deraedt, C., Pinaud, N., & Astruc, D. (2010). *Journal of the American Chemical Society, 136*, 12092–12098.
Eglinton, G., & Galbraith, A. R. (1956). *Chemistry & Industry, 38*, 737–738.
Fernandez, A. M., Munoz, M. O., Jaramillo, J. L., Mateo, F. H., & Gonzalez, F. S. (2010). *Advanced Synthesis and Catalysis, 352*(18), 3306–3320.
Gala, L., Lawson, M., Jomova, K., Zelenicky, L., Congradyova, A., Mazur, M., & Valko, M. (2014). *Molecules, 19*(1), 980–981.
Girard, C., Onen, E., Aufort, M., Beauviere, S., Samson, E., & Herscovici, J. (2006). *Organic Letters, 8*(8), 1689–1692.
Goh, W. Y. L., Chai, C. L. L., & Chen, A. (2014). *European Journal of Organic Chemistry, 10*, 7239–7244.
Guibal, E. (2005). *Progress in Polymer Science, 30*, 71–109.
Haron, M. J., Tiansih, M., Ibrahim, N. A., Kassim, A., & Wan Yunus, W. M. Z. (2009). *BioResources, 4*, 1305–1318.
Hassan, S., & Müller, T. J. J. (2015). *Advanced Synthesis and Catalysis, 357*(4), 617–666.
Huang, K., Xue, L., Hu, Y.-C., Huang, M.-Y., & Jiang, Y.-Y. (2002). *Reactive and Functional Polymers, 50*, 199–203.
Huisgen, R. (1963). *Angewandte Chemie, 75*(13), 604–637.
Islam, M. S., Mandal, B. H., Biswas, T. K., Rahman, M. L, Rashid, S. S., Tan, S. H., & Sarkar, S. M. (2016). *RSC Advances, 6*, 56450.
Jiang, Y., Kong, D., Zhao, J., Zhang, W., Xu, W., Li, W., & Xu, G. (2014). *Tetrahedron Letters, 55*(15), 2410–2414.
Jiang, H., Qin, S., Dong, H., Lei, Q., Su, X., Zhuo, R., & Zhong, Z. (2015). *Soft Matter, 11*, 6029–6036.
Kantam, M., Reddy, K., & Rajgopal, K. (2006). *Synlett*, 957–959.
Kim, J. Y., Park, J. C., Kang, H., Song, H., & Park, K. H. (2010). *Chemical Communications, 46*(3), 439–441.

Koganei, H., Tachikawa, S., E-Zaria, M. E., & Nakamura, H. (2015). *New Journal of Chemistry, 39,* 6388–6394.

Kuang, G. C., Michaels, H. A., Simmons, J. T., Clark, R. J., & Zhu, L. (2010). *Journal of Organic Chemistry, 75*(19), 6540–6548.

Lee, T., Cho, M., Ko, S. Y., Youn, H. J., Baek, D. J., Cho, W. J., . . . & Kim, S. J. (2007). *Medicinal Chemistry, 50,* 585.

Lipshutz, B. H., & Taft, B. R. (2006). *Angewandte Chemie International Edition, 118*(48), 8415–8418.

Masuyama, Y., Yoshikawa, K., Suzuki, N., Hara, K., & Fukuoka, A. (2011). *Tetrahedron Letters, 52*(51), 6916–6918.

Mnasri, N., Nyalosaso, J. L., Colacino, E., Derrien, G., Lamaty, F., Martinez, J., . . . & Charney, C. (2015). ACS sustain. *Chemical Engineering, 3*(10), 2516–2525.

O'Connell, D. W., Birkinshaw, C., & O'Dwyer, T. F. (2008). *Bioresource Technology, 99*(15), 6709–6724.

Pachón, L. D., Maarseveen, J. H. V., & Rothenberg, G. (2005). *Advanced Synthesis and Catalysis, 347*(6), 811–815.

Papadopoulou, M. V., Bloomer, W. D., Rosenzweig, H. S., Chatelain, E., Kaiser, M., Wilkinson, S. R., . . . & Ioset, J. R. (2012). *Journal of Medicinal Chemistry, 55*(11), 5554–5565.

Phan, N. T. S., Sluys, M. V. D., & Jones, C. W. (2006). *Advanced Synthesis and Catalysis, 348,* 609–679.

Prenesti, E., & Berto, S. (2002). *Journal of Inorganic Biochemistry, 88*(1), 37–43.

Rafiee-Moghaddam, R., Salimon, J., Haron, M. J., Jahangirian, H., Ismail, M. H. S., Afsah-Hejri, L., & Vafaei, N. (2014). *Digest Journal of Nanomaterials and Biostructures, 9*(1), 261–271.

Rahman, M. L., Rohani, N., Mustapa, N., & Yusoff, M. M. (2014). *Journal of Applied Polymer Science, 131*(19), 40833.

Rahman, M. L., Mandal, B. H., Sarkar, S. M., Yusoff, M. M., Arshad, S. E., & Baba, M. (2016). *Polymers for Advanced Technologies,* http://dx.doi.org/10.1002/pat.3840

Rahman, M. L., Mandal, H. B., Sarkar, S. M., Nor Asiken, A. W., Yusoff, M. M., Arshad, S. E., & Baba, M. (2016). *Fibers and Polymers, 4,* 521–532.

Rahman, M. L., Mandal, H. B., Sarkar, S. M., Kabir, M. N., Farid, E. M., Arshad, S. E., & Baba, M. (2016). *Journal of Macromolecular Science, 8*(Part A), 515–522.

Rajender, R. K., Uma, M. C., Rajgopal, K., & Lakshmi, K. M. (2008). *Synthetic Communications, 38*(13), 2158.

Reddy, K. R., Kumar, N. S., Sreedhar, B., & Kantam, M. L. (2006). *Journal of Molecular Catalysis A: Chemical, 252*(1), 136–141.

Rostovtsev, V. V., Green, L. G., Fokin, V. V., & Sharpless, K. B. (2002). *Angewandte Chemie International Edition, 114*(41), 2708–2711.

Roy, S., Chatterjee, T., Pramanik, M., Roy, A. S., Bhaumikd, A., & Islam Sk, M. (2014). *Journal of Molecular Catalysis A: Chemical, 386,* 78–85.

Sarkar, M. S., Sultana, T., Biswas, T. K., Rahman, M. L., & Yusoff, M. M. (2016). *New Journal of Chemistry, 40,* 497–502.

Siemsen, P., Livingston, R. C., & Diederich, F. (2000). *Angewandte Chemie International Edition, 39,* 2632–2657.

Silva, E. N., Jr., Barreto, R. F. S. M., Pinto, M. C. F. R., Silva, R. S. F., Teixeira, D. V., Souza, M. C. B. V., . . . & Pinto, A. V. (2008). *European Journal of Medicinal Chemistry, 43,* 1774.

Tang, W., & Becker, M. L. (2014). *Chemical Society Reviews, 43,* 7013–7039.

Tano, T., Mieda, K., Sugimoto, H., Ogura, T., & Itoh, S. (2014). *Dalton Transactions, 43,* 4871–4877.

Tavassoli, M., Isfahani, A. L., Moghadam, M., Tangestaninejad, S., Mirkhani, V., & Baltork, I. M. (2015). *Applied Catalysis A: Generalcat, 503,* 186–195.

Thomas, K. D. K., Adhikari, A. V., & Shetty, N. S. (2010). *European Journal of Medicinal Chemistry, 45*(9), 3803–3810.

Tornoe, C. W., Christensen, C., & Meldal, M. (2002). *Journal of Organic Chemistry, 67*(9), 3057–3064.

Wacharasindhu, S., Bardhan, S., Wan, Z.-K., Tabei, K., & Mansour, T. S. (2009). *Journal of the American Chemical Society, 131*(12), 4174–4175.

Wei, W.-L., Zhu, H.-Y., Zhao, C.-L., Huang, M.-Y., & Jiang, Y.-Y. (2004). *Reactive and Functional Polymers, 59,* 33.

Xia, Y., Fan, Z., Yao, J., Liao, Q., Li, W., Qu, F., & Peng, L. (2006). *Bioorganic & Medicinal Chemistry Letters, 16*(10), 2693–2698.

Yamada, Y. M. A., Sarkar, S. M., & Uozumi, Y. (2012). *Journal of the American Chemical Society, 134*(22), 9285–9290.

Zhang, X., Geng, Y., Han, B., Ying, M.-Y., Huang, M.-Y., & Jiang, Y. Y. (2001). *Polymers for Advanced Technologies, 12,* 642.