

# Catalytic application of second cycle copper-based laboratory waste for synthesis of beta-keto-1,2,3-triazole: A micro circular economy approach

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## ABSTRACT

This study follows the circular economy principle to explore the catalytic potential of second-cycle cuprous oxide laboratory waste. Undergraduate students generated cuprous oxide as a second cycle waste during a practical session, where they used an aqueous solution of recycled copper sulfate pentahydrate as a Fehling's reagent A. The cuprous oxide waste was isolated by a simple filtration method and characterized using infrared spectroscopy, powder X-ray diffraction, X-ray photoelectron spectroscopy, and electron microscopic techniques. The isolated material was used as an active click catalyst to synthesize beta-keto-1,2,3-triazole in an aqueous medium via a one-pot, three-component click reaction. The catalytic activity of the second-cycled cuprous oxide waste was compared with first-cycled cuprous oxide waste and commercial cuprous oxide. We observed that the catalyst was recycled and reused for up to two cycles without significant yield loss. Also, the synthesized beta-keto-1,2,3-triazole was found to show chelating properties towards copper.

## 1. Introduction

Cuprous oxide ( $\text{Cu}_2\text{O}$ ) is a p-type semiconductor with a band gap of 1.9–2.2 eV that absorbs light in the visible range of the electromagnetic spectrum and has been widely used in solar energy conversion [1], metal-insulator-metal resistive switching memory [2], Li-ion batteries [3], templating [4], gas sensing [5], water splitting [6], CO oxidation [7], and catalysis [8]. In health care, it is used as an antimicrobial material [9], and wound healing material [10]. In environmental applications, copper-based materials are known for preventing water from aerial microbial contamination [11], water disinfection [12,13], and wastewater treatment [14]. All these diverse applications of  $\text{Cu}_2\text{O}$ , have motivated many researchers globally to invest significant time and energy in developing different methods for synthesizing  $\text{Cu}_2\text{O}$ -based materials. Exploring the application of  $\text{Cu}_2\text{O}$  recovered from waste is highly valuable as it will support a circular economy, and green and sustainable development.

Following the principle of circular economy, recovering copper from various waste sources, and reusing it to the maximum possible number of cycles is important for pollution control and fulfilling the market demands. There are reports available where researchers have recovered copper from discarded electrical cables [15,16], and electronic appliances [17–24] in the present era of advanced technology and electronics. Similarly, several methods have been well-established for the

recovery of copper from industrial waste [25] and industrial wastewater [26–29]. However, very few reports appear on copper recovery from laboratory waste [30], which indicates that copper-based laboratory management towards a circular economy is yet to be explored.

In academic laboratories, at the school of chemical science or chemistry, reasonably large quantities of copper-based analytical reagents such as Fehling's reagent [31], Barfoed's reagent [32], and Benedict's reagent [33] are used for qualitative and quantitative estimation of reducing sugar. In all these analytical methods,  $\text{Cu}_2\text{O}$  is produced as a confirmatory test for reducing sugar which is discarded as waste. Looking at the diverse functional properties of  $\text{Cu}_2\text{O}$ , this waste can be easily accepted as a resource and can be applied as a functional material in different fields. Hence, the creative use of waste to achieve a different target without any investment in fresh resources will help us develop a micro-circular economy practice and wise laboratory waste management.

The click catalytic potential of Cu-based material was immensely explored in the last few decades immediately after the discovery of click reaction by Meldal [34], and Sharpless [35]. Click reactions are applied to synthesize triazole-based functional organic compounds such as pharmaceuticals [36], agrochemicals [37], polymers [38], dyes [39], dendrimers [40], chemosensors [41], and others. The most commonly used Cu-based catalyst for click reaction is the Cu(II)-ascorbate system, where *in-situ* generated Cu(I) participates in click reaction [35]. Other

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Cu-based click catalysts include cupric sulfide (CuS) [42], cupric oxide (CuO) [43], Cu(I)-zeolite [44], Cu-coordination complex [45,46], polymer-supported Cu(I) [47], graphene-supported Cu<sub>2</sub>O nanoparticles (NPs) [48], charcoal-supported Cu<sub>2</sub>O NPs [49], Magnetic Fe<sub>3</sub>O<sub>4</sub>@-TiO<sub>2</sub>/Cu<sub>2</sub>O [50], Cu NPs [51], Cu<sub>2</sub>O NPs [52], and Cu-cluster [53]. All these Cu-based materials have been reported as excellent catalysts for click reactions. But to obtain such an efficient catalyst, there is a requirement of investment, which leads to the consumption of resources. From an environmental and circular economy viewpoint, it will always be inspiring if a catalyst with a comparable catalytic potential is obtained from waste.

The catalytic application of waste-derived Cu-based materials toward organic synthesis is yet to be explored and has a wide future scope towards the sustainable development of various Cu-catalyzed organic synthetic procedures. In this study, Cu<sub>2</sub>O was recovered from second-cycle laboratory waste, which undergraduate student produced during their practical session. The isolated Cu<sub>2</sub>O was used as an efficient catalyst for synthesizing a variety of  $\beta$ -keto-1,2,3-triazole via a one-pot three-component click reaction in an aqueous medium. We demonstrated the simplest possible way to increase the overall life cycle of copper-based reagents used in academic laboratories and the upcycling of generated waste in academic laboratories.

## 2. Materials and Methods

### 2.1. Materials

Cu<sub>2</sub>O was isolated from laboratory waste by extrication at its source. Organic precursor; 2-Bromoacetophenone (C<sub>6</sub>H<sub>5</sub>COCH<sub>2</sub>Br, 98 %), 2-Bromo-4'-methylacetophenone (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>Br, 90 %), 2-Bromo-4'-methoxyacetophenone (CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>Br, 97 %), phenylacetylene (C<sub>6</sub>H<sub>5</sub>CCH, 98 %), 4-Ethynyltoluene (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CCH, 97 %), 3-Ethynyltoluene (CH<sub>3</sub>C<sub>4</sub>H<sub>4</sub>CCH, 97 %), 1-Ethynyl-4-fluorobenzene (FC<sub>6</sub>H<sub>4</sub>CCH, 99 %), 1-Ethynyl-3,5-difluorobenzene (F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CCH, 97 %), propargyl alcohol (HCCCH<sub>2</sub>OH, 99 %), 2-Methyl-3-butyn-2-ol (HCCC(CH<sub>3</sub>)<sub>2</sub>OH, 98 %), 1-Octyne (CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CCH, 97 %), were purchased from Sigma Aldrich, India. Sodium azide (NaN<sub>3</sub>, 99 %), anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, 99 %), solvents such as ethyl acetate (CH<sub>3</sub>COOCH<sub>2</sub>CH<sub>3</sub>, 98 %), and hexane (C<sub>6</sub>H<sub>14</sub>, 98 %), and silica (60–120 mesh) were purchased from Loba Chemie Pvt. Ltd., India. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and H<sub>2</sub>O<sub>2</sub> (30 %) were purchased from Fischer Scientific, India. All these organic precursors, reagents, and solvents were used as received. Distilled water was used as a reaction medium for all catalytic reactions.

### 2.2. Characterization

The Fourier transform infrared (FT-IR) spectrum of Cu<sub>2</sub>O was recorded using FT/IR-6X FTIR Spectrometer. Powder X-ray diffraction (PXRD) of Cu<sub>2</sub>O powder was performed in a Bruker D8 Avance instrument with Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation in reflection mode. X-ray photoelectron spectroscopy (XPS) analysis was carried out using X-ray photoelectron spectrometer (SPECS, Germany). The morphology and surface features of the sample were recorded using FEI Quanta 200 Scanning electron microscope (SEM), and high-resolution transmission electron microscope (HRTEM), JEOL JEM-2100 Plus. Nuclear resonance spectroscopy (NMR) and high-resolution mass spectroscopy (HR-MS) techniques were used to characterize the final organic products. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using Bruker Avance 400 or 500 MHz NMR instrument, and the HR-MS were recorded using a High-Resolution Q-ToF Mass spectrometer. IR spectra of 1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one were recorded using Bruker Alpha II spectrometer at attenuated total reflectance (ATR) mode.

### 2.3. Isolation of waste Cu<sub>2</sub>O

Our undergraduate students generated second cycle waste Cu<sub>2</sub>O

**Table 1**

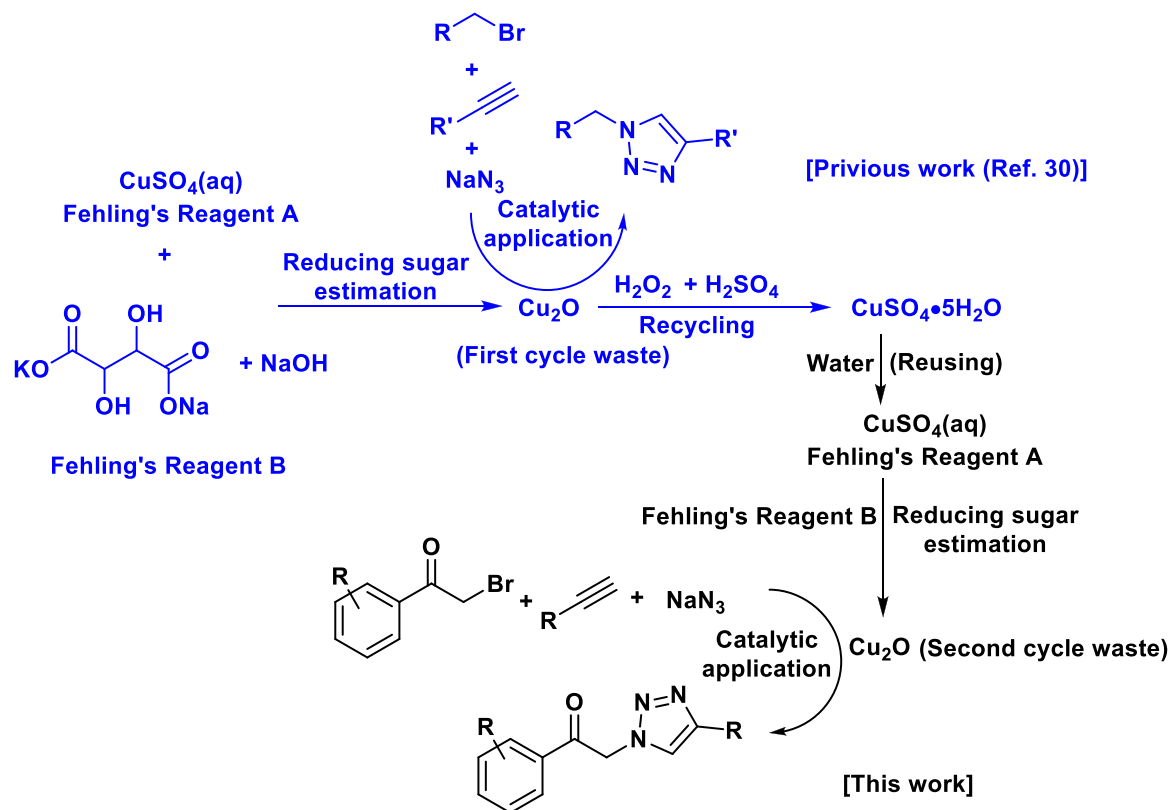
Comparison of upcycling of copper-based function materials from different waste sources.

Source	Copper-based materials	Used as a/an	Reference
Waste electrical cables	Cu <sub>2</sub> O@Graphene	mercury and dopamine sensor	[15]
Waste electrical cables	Cu <sub>2</sub> O NPs	-	[16]
E-waste	Cu	antibacterial agent	[18]
E-waste	Cu	-	[19]
E-waste	Cu(EDTA)-Complex	-	[20]
E-waste	Cu	-	[21]
E-waste	Cu	-	[22]
E-waste	Cu and CuO NPs	(1) antimicrobial agent and (2) photocatalyst for Rhodamine B decomposition.	[23]
E-waste	Cu-Sn NPs	-	[61]
E-waste	Cu-Cu <sub>2</sub> O NPs	catalytic for textile dye (RB4) decomposition	[57]
E-waste	Cu NPs	antimicrobial agent	[55]
E-waste	Cu@C	catalyst for Rhodamine B decomposition.	[58]
E-waste	Cu NPs	catalyst for surfactant decomposition.	[59]
E-waste	Cu NPs	antifouling agent	[56]
E-waste	CuO@C	electrode material for ascorbic acid detection.	[24]
Metallurgical waste	Cu	catalyst for CO <sub>2</sub> reduction	[60]
Industrial waste	CuSO <sub>4</sub>	-	[25]
Industrial wastewater	Cu	-	[26]
Industrial wastewater	Cu	-	[27]
Industrial wastewater	Cu@C	-	[28]
Industrial wastewater	Cu	-	[29]
Laboratory waste	Cu <sub>2</sub> O	catalyst for the synthesis of a regioselective 1,4-disubstituted triazole	[30]
Copper industry	Cu-flakes	catalyst for reductive actamidation of nitroarenes	[72]
Second-cycle laboratory waste	Cu <sub>2</sub> O	catalytic for the synthesis of $\beta$ -keto-1,2,3-triazole	This work

during their practical session where they were assigned an experiment, a quantitative estimation of reducing sugar in an unknown sample using Fehling's reagents (Detailed experimental procedure is described in [supporting information](#)). Fehling's solution A for those experiments, was prepared by making use of recycled CuSO<sub>4</sub>·5H<sub>2</sub>O from our previous work [30]. In this reaction, Cu<sub>2</sub>O was formed as second-cycle waste, which was stored in separate containers by the cooperation of students. After the class, Cu<sub>2</sub>O was filtered using Whatman filter paper, washed with water thrice (3 × 10 mL), and air dried for 24 hours. The amount of isolated Cu<sub>2</sub>O was found to be 9.23 g.

### 2.4. General procedure for one-pot synthesis of $\beta$ -keto-1,2,3-triazole

2-bromoacetophenone derivative (1 mmol), sodium azide (1.2 mmol), terminal alkyne (1.2 mmol), Cu<sub>2</sub>O (5 mol%), and water (5 mL) were taken in a 50 mL round-bottom flask. The reaction mixture was stirred on a magnetic stirrer at 100 °C at 600–800 rpm for 1 h. The progress of the reaction was monitored visually by the formation of an insoluble solid cake. Using a separating funnel, the product was isolated in ethyl acetate (3 × 10 mL). The aqueous layer holding soluble ions and catalyst particles was transferred to a separate container. The organic layer was transferred to a 100 mL beaker, dried by adding anhydrous



**Scheme 1.** Schematic representation of micro circular economy of copper-based laboratory waste.

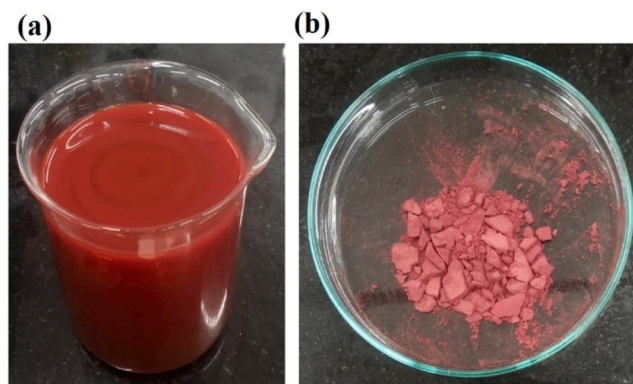
$\text{Na}_2\text{SO}_4$ , and filtered. The ethyl acetate was evaporated and the obtained crude product was purified by column chromatography using silica gel (60–120 mesh), as a stationary phase and different ratios of hexane-ethyl acetate as an eluent. The identities of the isolated pure compounds were confirmed by recording  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and ESI-HRMS.

### 3. Results and discussion

#### 3.1. Cu-circular economy

In modern society, for maintaining a continuous supply of copper, many researchers have developed different methods to recover copper from various waste sources to increase the net life cycle of copper. In the last few decades, multiple methods for copper recovery from electronic waste (e-waste), industrial waste, and wastewater were developed (Table 1). Many researchers have also successfully upcycled Cu-based functional materials from several waste sources via a synergetic approach (Table 1). Abdelbasir et al., and group synthesized  $\text{Cu}_2\text{O}$  NPs from waste electrical cables and successfully fabricated  $\text{Cu}_2\text{O}$  NPs on graphene as an economical and eco-friendly electrochemical sensor for mercury [15,16]. Sinha et al., recovered copper from e-waste and used it as an antibacterial agent [18]. Similarly, few researchers reported the synthesis of copper nanoparticles from recovered copper from e-waste and their antimicrobial activity [23,55,56]. Few reports claim the synthesis of copper-based nanoparticles and their catalytic potential in environmental remediation [23,57–59]. Copper recovered from metallurgical waste showed appreciable catalytic potential toward reducing carbon dioxide to carbon monoxide [60]. Mathaiyan et al. transformed copper recovered from e-waste to  $\text{CuO}@C$  for electrode material and was used for non-enzymatic ascorbic acid detection [24]. The application of copper and copper-based materials derived from various waste sources as a catalyst in organic synthesis is yet to be explored.

The circular economy practice in academic and research laboratories will help motivate the coming generation to walk toward reduce-reuse



**Fig. 1.** Photograph of (a) second-cycle copper-based laboratory waste generated by undergraduate students during their practical session, and (b) isolated  $\text{Cu}_2\text{O}$  powder.

and recycle. Our previous work recovered copper from  $\text{Cu}_2\text{O}$ -laboratory waste as  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  via chemical treatments with 97 % Cu recovery [30]. The recovered  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  was reused by our new batch of students as Fehling's reagent A, during a practical session and the second cycle waste  $\text{Cu}_2\text{O}$  was generated (Scheme 1). Fehling's reagent preparation and experimental procedure are described in supporting information. The waste was separated at the source and collected in separate containers. After the class, the  $\text{Cu}_2\text{O}$  was isolated by simple filtration using Whatman filter paper, washed with water, and air-dried (Fig. 1).

#### 3.2. Characterization of second cycle waste $\text{Cu}_2\text{O}$

In the IR spectrum of isolated  $\text{Cu}_2\text{O}$  (Fig. 2a), the peak at  $620\text{ cm}^{-1}$  is due to Cu-O stretching. The peak at  $1630\text{ cm}^{-1}$  corresponds to the

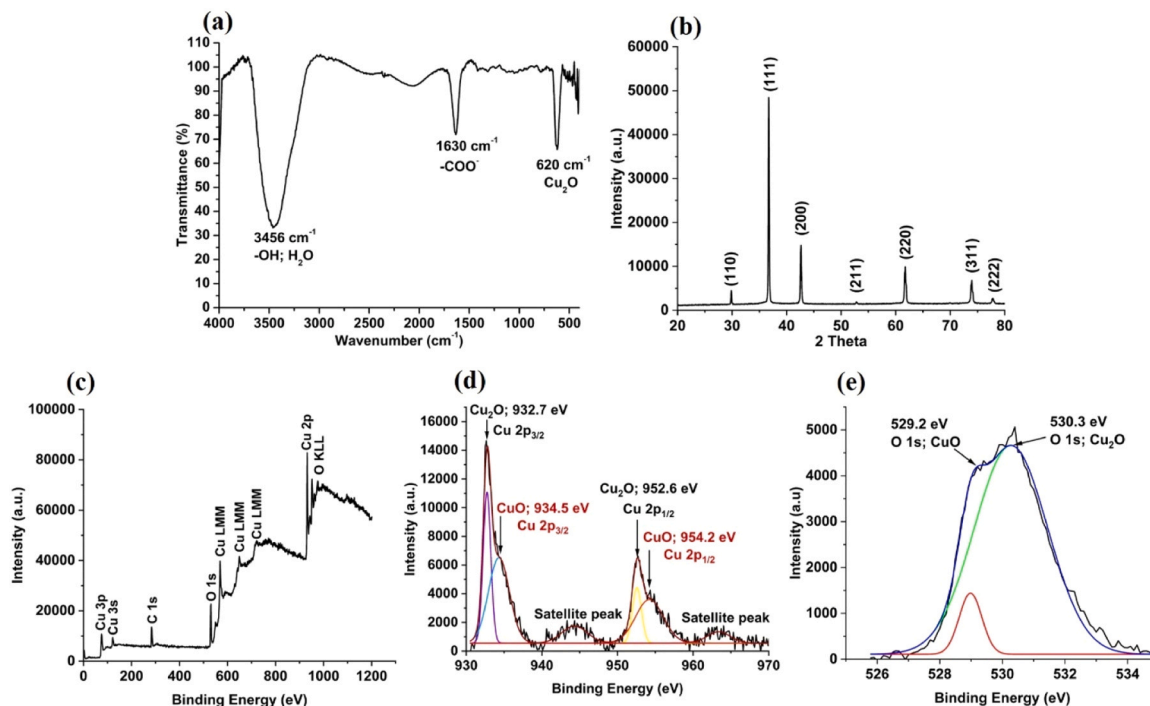


Fig. 2. Characteristic features of isolated  $\text{Cu}_2\text{O}$  (a) FTIR, (b) PXRD, XPS (c) survey spectrum, (d) Cu 2p spectrum, and (e) O 1s spectrum.

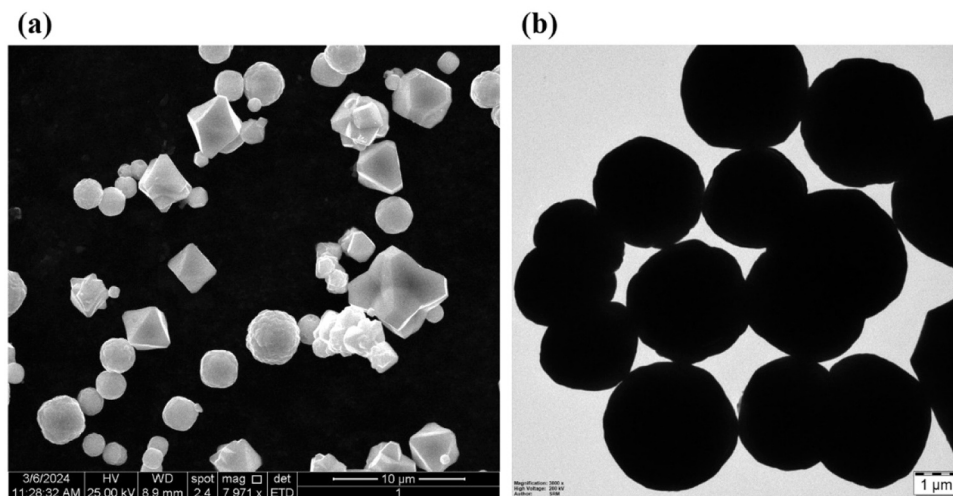


Fig. 3. Electron microscope images (a) SEM and (b) TEM.

carboxylate ( $-\text{COO}^-$ ) functional group of the adsorbed tartrate (from Fehling's reagent B) and/or gluconate (oxidized product of glucose) on  $\text{Cu}_2\text{O}$ . The peak at  $3456\text{ cm}^{-1}$  refers to the stretching frequency of the hydroxyl ( $-\text{OH}$ ) group of tartrate, gluconate, and moisture on  $\text{Cu}_2\text{O}$ . PXRD shows the characteristic Bragg's reflection at 29.8, 36.6, 42.6, 52.8, 61.7, 73.9, and 77.8 which referred to (110), (111), (200), (211), (220), (311), and (222) Miller plane respectively in  $\text{Cu}_2\text{O}$  (Fig. 2b). The obtained data are in good agreement with the reported data in the literature [30,52]. The purity of the waste  $\text{Cu}_2\text{O}$  was further investigated by XPS analysis. Full survey scan spectrum (Fig. 2c), shows a binding energy peak at 75.8, 121.8, 284.8, 529.8, and 931.8 eV corresponding to copper (Cu 3p), copper (Cu 3s), carbon (C 1s), oxygen (O 1s) and copper (Cu 2p) respectively. In the Gaussian-fitted expanded copper 2p spectrum, binding energy peaks at 932.7 eV and 952.6 eV corresponding to  $\text{Cu } 2p_{3/2}$  and  $\text{Cu } 2p_{1/2}$  respectively confirm that the oxidation state of the copper in the sample is  $\text{Cu}^+$  (Fig. 2d). Additionally, binding

energy peaks at 934.5 eV ( $\text{Cu } 2p_{3/2}$ ) and 954.2 eV ( $\text{Cu } 2p_{1/2}$ ) corresponds to trace amounts of  $\text{Cu}^{2+}$  as an impurity. The core level O 1s peak for  $\text{Cu}_2\text{O}$  was observed at 530.3 eV and that of CuO was observed at 529.2 eV. All these binding energy data confirm that the sample is  $\text{Cu}_2\text{O}$  with a trace amount of CuO as an impurity. The obtained results agree with the reported data in the literature [30,52,54]. Detection of a trace amount of CuO as an impurity may be due to aerial oxidation of the surface of  $\text{Cu}_2\text{O}$  to CuO. Another possibility could be the overheating of Fehling's solution during the experiment in the presence of insufficient glucose. Electron microscopic images show that the particle size of  $\text{Cu}_2\text{O}$  is 1–5  $\mu\text{m}$  with different shapes and morphology (Fig. 3). This difference in the shape and morphology of the  $\text{Cu}_2\text{O}$  particles is possibly due to the absence of stabilizing agents or any morphology-directing agents in the reaction medium. Another possible parameter could be a high reaction temperature (70  $^\circ\text{C}$ ), due to which the reaction was completed within minutes. Therefore, due to the absence of a morphology direction agent

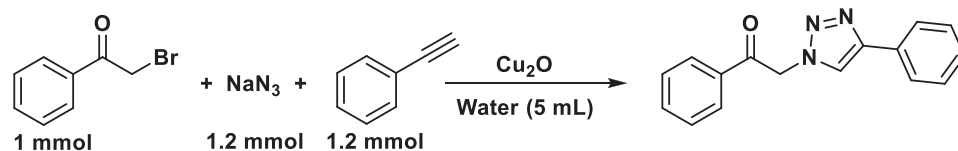
**Table 2**

Comparison of our work with the methods reported in the literature for the click synthesis of 1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one.

Catalyst	No. of steps involved in catalyst preparation	Solvent	Reaction temperature (C)	Reaction time	Yield (%)	Reference
nano-Fe <sub>3</sub> O <sub>4</sub> @TiO <sub>2</sub> /Cu <sub>2</sub> O	3	Water	Reflux	20 mins	89	[50]
CuI-AK	2	Water	Reflux	20 mins	84	[63]
Poly(4-vinylpyridine)-CuI	1	Water	Reflux	25 mins	89	[65]
Cu/Cu(OTf) <sub>2</sub>	-	Water	85; (microwave irradiation)	10 mins	92	[67]
CuI	-	Water	Room temperature	8 h	81	[68]
CuI/SMI-TD	2	Water	Reflux	20 mins	78	[64]
CuCl	-	Ionic liquid	25	10 mins	90	[69]
CuI-Polymer	1	Acetonitrile	Reflux	1 h	89	[66]
<b>Cu<sub>2</sub>O waste</b>	-	<b>Water</b>	<b>100</b>	<b>1 h</b>	<b>91</b>	<b>This work</b>

**Table 3**

Optimization of three-component click synthesis of 1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one.



Entry	Catalyst (Cu <sub>2</sub> O)	Mole %	Temperature C	Time (h)	Yield (%) <sup>a</sup>
1	Commercial	1	RT	24	17
2	First cycle	1	RT	24	19
3	Second cycle	1	RT	24	11
4	Commercial	5	RT	24	75
5	First cycle	5	RT	24	69
6	Second cycle	5	RT	24	73
7	Commercial	1	100	1	59
8	First cycle	1	100	1	70
9	Second cycle	1	100	1	61
10	Commercial	2	100	1	81
11	First cycle	2	100	1	78
12	Second cycle	2	100	1	83
13	Commercial	5	100	1	95
14	First cycle	5	100	1	93
15	Second cycle	5	100	1	91

RT: Room temperature.

<sup>a</sup> Isolated yield

and high reaction rate, the control over the morphology is lost and particles of different shapes and sizes are formed. Several researchers have reported, morphology-controlled synthesis of Cu<sub>2</sub>O at room temperature for a longer reaction time (a few hours) in the presence of stabilizing agents or morphology-directing agents such as cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and poly(vinyl pyrrolidone) (PVP) [62].

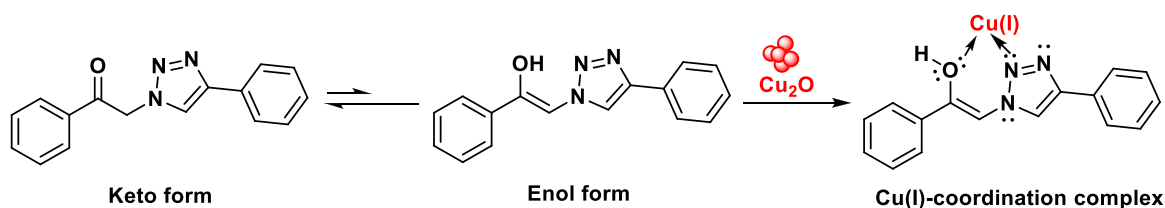
### 3.3. Catalytic application of second cycle waste Cu<sub>2</sub>O

For the synthesis of β-keto-1,2,3-triazole, many researchers have invested significant resources to develop an efficient catalyst (Table 2). Nano-Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub>/Cu<sub>2</sub>O catalyst was developed by Nemat et al., by making use of ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), tetra butyl titanate (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>), and cupric chloride (CuCl<sub>2</sub>) as a core metal precursor and several other solvent and reagents in three steps [50]. Mirsafaei et al., first coated 3-aminopropyltriethoxysilane on mesoporous silica by refluxing these mixtures in toluene under a nitrogen atmosphere for 24 h. In the second step, they reflux the resulting mass and CuI in acetonitrile for 5 h under a nitrogen atmosphere to obtain the desired catalyst [63]. Similarly, Ebrahimpour-Malamir et al., synthesized a copper-based click catalyst by modification of styrene-co-maleic anhydride in two steps [64]. A few other polymer-supported click catalysts include CuI@poly(4-vinyl pyridine) [65], and CuI@amberlyst A-21 [66]. Fazeli, et al., synthesized β-keto-1,2,3-triazole under microwave irradiation by making use of a mixture of Cu (10 mol%) and Cu

(OTf)<sub>2</sub> (10 mol%) as a catalyst [67]. CuI alone was also reported to show good catalytic activity for the synthesis of β-keto-1,2,3-triazole [68]. CuCl is reported as a good catalyst in ionic liquid [69]. Looking at the efficient catalytic potential of Cu(I)-based material, and to promote a circular economy practice in academia we used second-cycled Cu<sub>2</sub>O waste as a catalyst for the synthesis of β-keto-triazole in water.

Initially, to test the catalytic potential of the second-cycled Cu<sub>2</sub>O-waste, 2-bromoacetophenone (1 mmol), sodium azide (1.2 mmol), phenylacetylene (1.2 mmol), and Cu<sub>2</sub>O (1 mol%) were taken in 50 mL round-bottom flask. 5 mL water was added to it and kept on a magnetic stirrer at 600–800 rpm for 24 h. Different sets of reactions were performed to optimize the reaction condition by varying different reaction parameters such as catalyst mole percentage, reaction time, and temperature (Table 3). The reaction progress was observed visually by forming a solid cake. The optimum reaction condition for the synthesis of β-keto-1,2,3-triazole was found to be 5 mol% of the catalyst, 100 °C reaction temperature for 1 hour's reaction time. The same reaction was performed with commercial Cu<sub>2</sub>O and first-cycle Cu<sub>2</sub>O waste and their catalytic activity was found to be almost the same. This result is a clear indication that copper can be recycled multiple times from Fehling's reaction and depending upon the other requirements, it can be used as a catalyst to carry out desired organic transformations.

Compared to our previous report [30], we synthesized 1,4-disubstituted 1,2,3-triazole (nonchelating 1,2,3-triazole) using first-cycle Cu<sub>2</sub>O waste as a catalyst. The reaction was working at room temperature, whereas in present studies at room temperature, the reaction was slow



Scheme 2. Schematic representation of 1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one complex formation with  $\text{Cu}_2\text{O}$  catalyst.

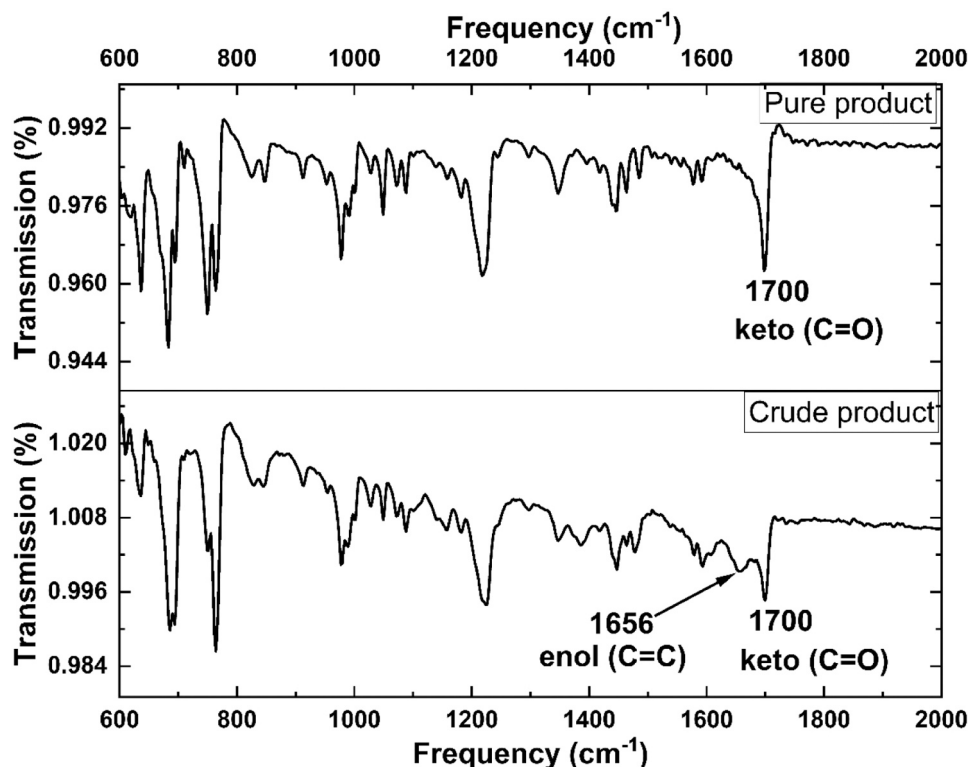


Fig. 4. FT-IR Spectra of crude product and pure product.

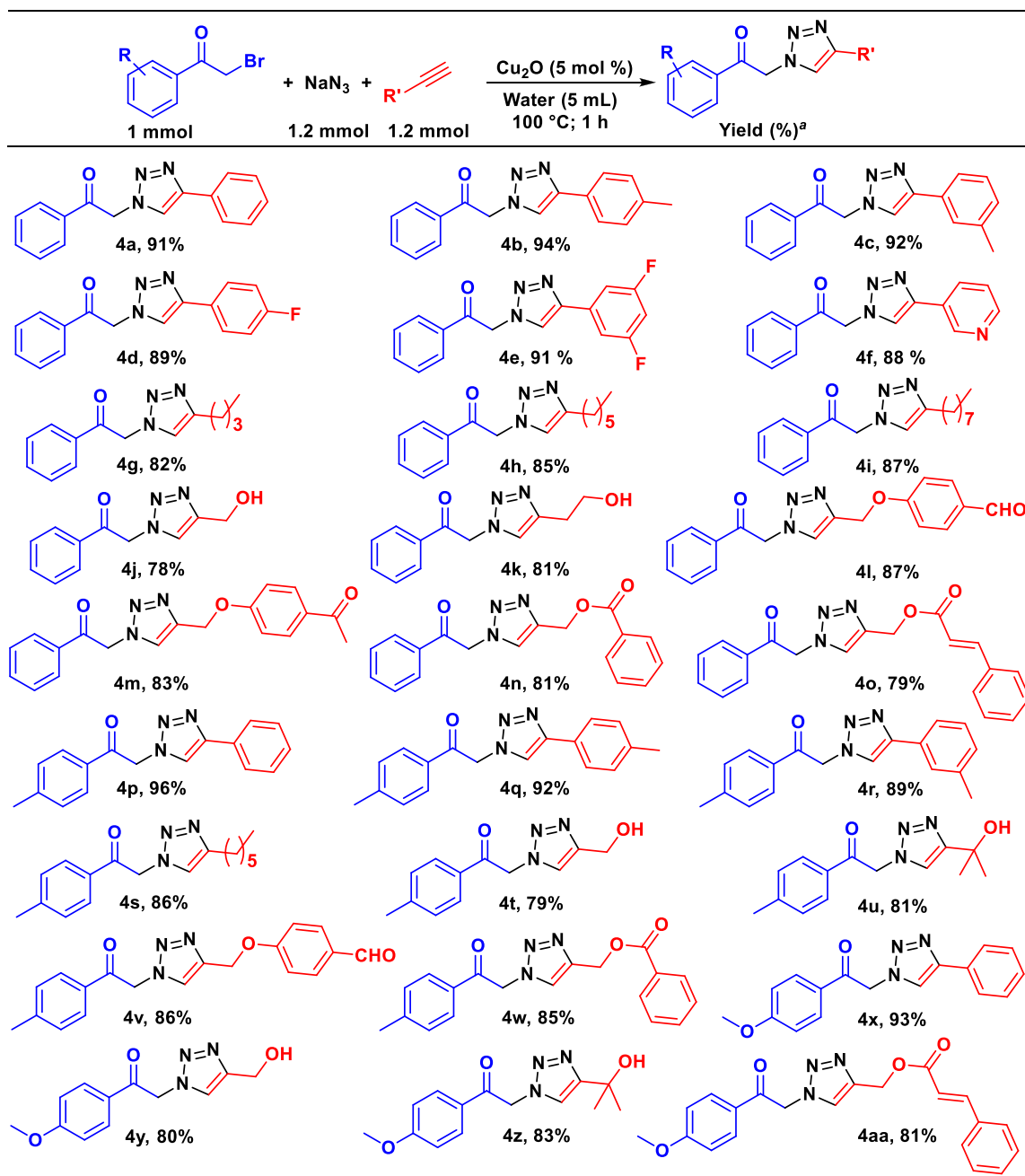
with poor yield (Table 3). To increase the reaction rate and to obtain a reasonably good yield of the product, the reaction temperature was raised to 100 °C. The high-temperature requirement in the present case may be due to the chelating ligand nature of the product ( $\beta$ -keto-1,2,3-triazole). As the  $\beta$ -keto-1,2,3-triazole contain  $\alpha$ -proton, it undergoes keto-enol tautomerism and gets adsorbed on the catalyst's surface via chelation (Scheme 2). Due to chelation of the product on the surface of the catalyst, fewer active sites are available for the next catalytic cycle, which reduces the reaction rate. After the completion of the reaction, the extracted crude product was found to be light blue. This indicates that the copper from the catalyst and the  $\beta$ -keto-1,2,3-triazole have probably formed a chelated coordination complex. The formation of the chelated coordination complex was further confirmed by recording the FT-IR spectra of the crude product and the purified product. In the IR spectrum of the crude product, the  $\text{C}=\text{C}$  stretching frequency at  $1656\text{ cm}^{-1}$  corresponding to enol was observed along with the ketone ( $\text{C}=\text{O}$ ) stretching frequency at  $1700\text{ cm}^{-1}$ . Whereas in the IR spectra of a pure product, the stretching frequency corresponding to ketone ( $1700\text{ cm}^{-1}$ ) was observed (Fig. 4), and no trace of enol was found. Due to the chelation of the products with the catalyst, most of the catalytic synthesis of  $\beta$ -keto-1,2,3-triazole is reported under reflux conditions.

With the optimized reaction condition, the substrate scope of the reaction was extended to various other bromoacetophenone derivatives and structurally diverse terminal acetylene. The presence of different

functional groups (alcohol, ether, ester, aldehyde, ketone, and alkene) on either substrate did not affect the product formation (Table 4).

Using  $\text{Cu}_2\text{O}$  waste as an active catalyst has an added advantage, as it reduces the operational cost involved in catalyst synthesis, and promotes waste management and a circular economy. Such waste-derived catalysts can be wisely used to synthesize various bioactive compounds.  $\beta$ -keto-1,2,3-triazole based organic skeletons are important for drug evolution viewpoint. Few researchers reported the anti-cancer activity of  $\beta$ -keto-1,2,3-triazole molecules against various cancerous cells [68, 70, 71]. In this study, we report the efficient synthesis of 1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (Table 4, 4a), 1-phenyl-2-(4-(*p*-tolyl)-1H-1,2,3-triazol-1-yl)ethan-1-one (Table 4, 4b), 2-(4-hexyl-1H-1,2,3-triazol-1-yl)-1-phenylethan-1-one (Table 4, 4i), 2-(4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)-1-phenylethan-1-one (Table 4, 4j), 2-(4-phenyl-1H-1,2,3-triazol-1-yl)-1-(*p*-tolyl)ethan-1-one (Table 4, 4p), and 1-(4-methoxyphenyl)-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (Table 4, 4x). All these  $\beta$ -keto-1,2,3-triazole compounds are known to show anti-cancer activity against lung, colon, and cervical cancer at modest doses (Table 5) [68]. Vantikommu et al. synthesized all these  $\beta$ -keto-1,2,3-triazole compounds using CuI as a catalyst. Applying copper-based waste as a catalyst for synthesizing useful compounds will lead to green and sustainable waste management, circular economy, pollution control, and overall cost reduction of valuable products.

Table 4

Cu<sub>2</sub>O catalyzed one-pot three-component click reaction of sodium azide, bromoacetophenone derivatives, and terminal acetylene.<sup>a</sup>Isolater yield

Copper and copper-based materials are also known for their biological properties [9,10]. The formation of a chelate complex of this bio-active  $\beta$ -keto-1,2,3-triazole [68] with copper opens a door for another research area to explore the synergetic effect of Cu and  $\beta$ -keto-1,2,3-triazole on a different area of biochemistry. The chelating properties of  $\beta$ -keto-1,2,3-triazole could also be points of interest for supramolecular chemists, and material chemists.

### 3.4. Proposed mechanism for one-pot three-component click reaction

In the first step, a substitution reaction occurs between 2-bromo-ketone and NaN<sub>3</sub>, forming 2-azido-ketone or  $\beta$ -keto azide (Scheme 3). In-

situ formed  $\beta$ -keto azide gets adsorbed on the surface of the catalyst via a coordination bond. Simultaneously, oxidative addition of the terminal alkyne takes place on the surface of a catalyst and results in the copper-acetylide complex. The oxidation state of the participating copper changes from Cu(I) to Cu(II). Following this, cycloaddition between  $\beta$ -keto azide and terminal acetylene takes place. In the last step, reductive elimination results in the desired product formation. Other researchers have also reported a similar mechanism involving the formation of a copper-azide complex and copper-acetylide complex, resulting in a complex intermediate involved in copper-catalyzed azide-alkyne cycloaddition reactions [73].

**Table 5**

Anticancer activity of our synthesized compounds reported in the literature [68].

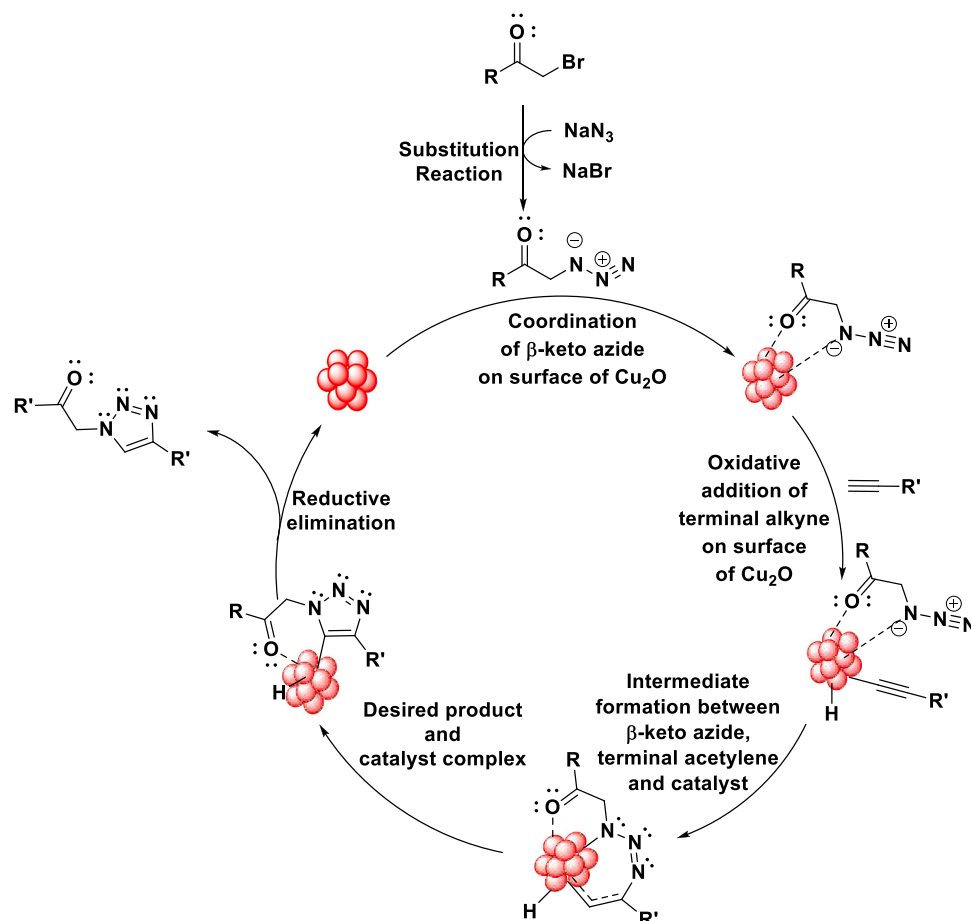
Compounds (Table 4)	Cytotoxicity (IC <sub>50</sub> μM)		
	A549 (Lung Cancer)	HT-29 (Colon Cancer)	He La (Cervical Cancer)
4a	> 300	> 300	> 300
4b	292	238	> 300
4i	> 300	> 300	> 300
4j	> 300	> 300	> 300
4p	> 300	> 300	> 300
4x	> 300	49	> 300

### 3.5. Recyclability and leaching test of the catalyst

In heterogeneous catalysis, the catalyst's reusability and leaching are important parameters to be evaluated. The recyclability of the catalyst was examined by synthesizing 1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (Table 4; 4a) by following our previous procedure [30]. The catalyst was reused for up to two cycles without significant product yield loss (Table 6). The poor reusability of the catalyst could be due to the chelating property of the product with the catalyst, resulting in the formation of a coordination complex with the catalyst (Scheme 2, Fig. 4.). The possible characteristic change in the catalyst was also examined through PXRD, and XPS analysis after the second catalytic cycle (Fig. 5.). In the PXRD spectrum, the Bragg's reflection peaks corresponding to (111), (200), (220), and (311) miller plane of Cu<sub>2</sub>O were observed with low intensity compared to that of unused Cu<sub>2</sub>O (Fig. 2b). Additionally, several intense peaks from 9.5 to 33.6 were observed, which may be the characteristic feature of Cu

(I)-1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one complex. To authenticate this observation, a separate experiment was performed where 14 mg of Cu<sub>2</sub>O and 26 mg of pure 1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (4a) was taken in a round-bottom flask containing 20 mL ethyl acetate and stirred magnetic stirrer for 4 hours at room temperature. The progress of the complexation reaction was observed by the change in color of Cu<sub>2</sub>O (orange-red) to blue. Further, the solvent was evaporated, and the Cu-complex was dried. In the PXRD spectrum of the obtained Cu-complex, a new set of peaks was observed, which also matches the additional peaks present in the PXRD spectra of the used catalyst after the second cycle (Fig. 5a). In the XPS summary scan, the C 1 s peak at 284.8 eV appears more intense (Fig. 5b) than the C 1 s peak intensity of unused catalysts (Fig. 2c). The increase in the relative intensity of the C 1 s peak may be due to coordinated β-keto-1,2,3-triazole on the surface of the used catalyst. Additionally, a binding energy peak at 399.8 eV corresponding to nitrogen (N 1 s), can be assigned to the nitrogen of the triazole ring. In the high-resolution Cu 2p spectrum, characteristic binding energy peaks corresponding to Cu(I) and Cu(II) were observed. In the O 1 s, spectrum, the peak at 529.3 eV and 530.6 eV corresponds to the O in CuO and Cu<sub>2</sub>O observed (Fig. 5c). Additionally, a low-intensity peak at 533 eV and 534 eV can be assigned to enolate oxygen in Cu-β-keto-1,2,3-triazole complex and keto oxygen of β-keto-1,2,3-triazole respectively (Fig. 5d).

To examine the copper leaching during the catalytic reaction, 7.1 mg (5 mol%) of Cu<sub>2</sub>O was taken in a 50 mL round-bottom flask containing 5 mL water and heated at 100 °C with continuous stirring for 1 h. Following this, the Cu<sub>2</sub>O was filtered using Whatman filter paper. The filtrate was transferred to another 50 mL round-bottom flask and 2-Bromoacetophenone (1 mmol), NaN<sub>3</sub> (1.2 mmol), and phenylacetylene (1.2 mmol) were added to it. The reaction mixture was heated at 100 °C



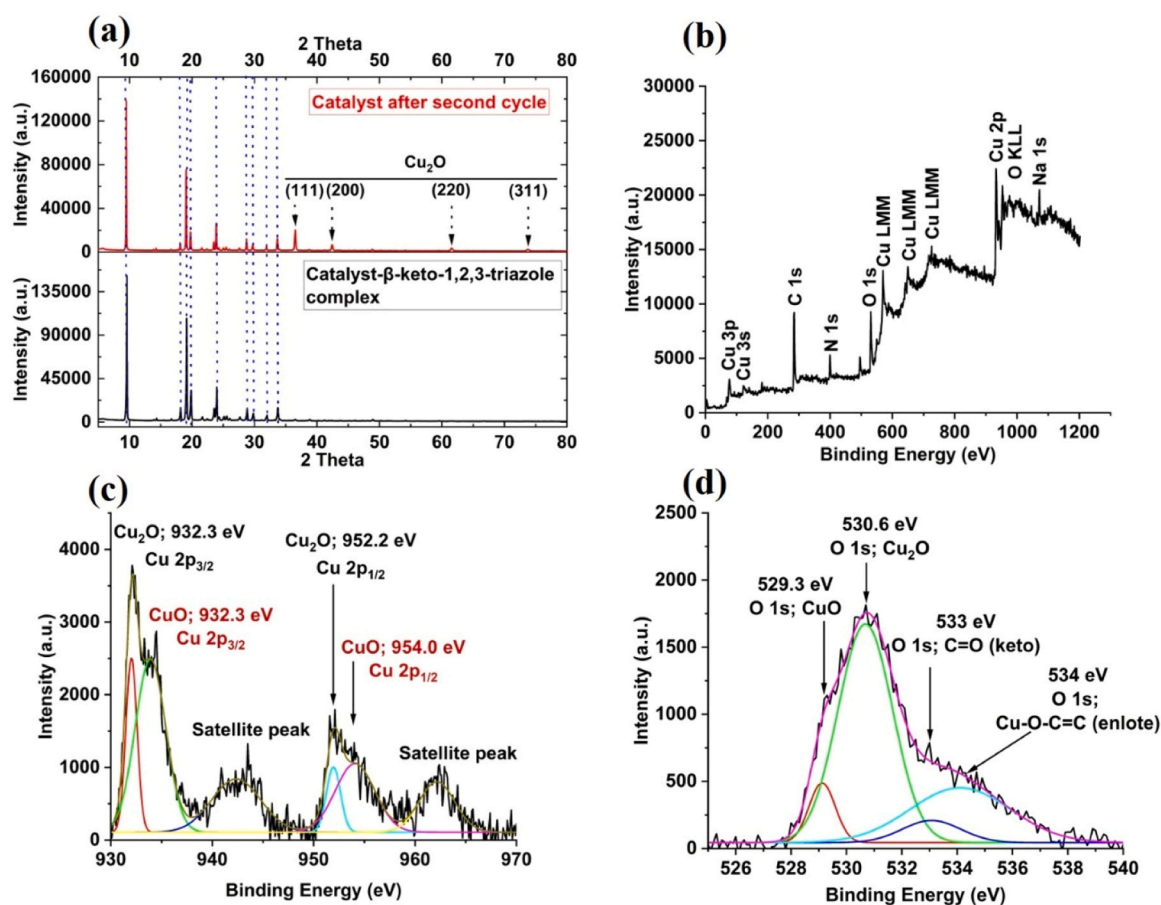
**Scheme 3.** Proposed mechanism for synthesis of β-keto-1,2,3-triazole.



**Table 6**  
Recycling results of Cu<sub>2</sub>O catalyst.

Run	Yield (%) <sup>a</sup>
1	92
2	83
3	56

<sup>a</sup> Isolated yield.



**Fig. 5.** (a) XRD of the catalyst after the second cycle and Cu-(1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one) complex. XPS spectra of the catalyst after the second cycle (b) survey spectrum, (c) Cu 2p spectrum, and (d) O 1s spectrum.

with continuous stirring for 1 h. The organic component of the reaction mixture was extracted in ethyl acetate and analyzed via TLC and light spot corresponding to the desired product was observed along with the starting materials. The product was purified via column chromatography, the obtained yield was found to be 13.4 % (35.3 mg). This result indicates that the copper leaching takes place at 100 °C and the leached-out copper also participates in the reaction as a homogeneous catalyst. Mostly Cu<sub>2</sub>O acts as a heterogeneous catalyst and leached out copper in the reaction medium acts as a homogeneous catalyst. The same reaction was performed for the second time with the aqueous component after completion of the first leaching test experiment, and no trace of the product formation was observed. This clearly shows that the leached-out

copper after catalyzing the reaction, formed a coordination complex with the product and gets extracted in ethyl acetate, and copper availability in the aqueous component is not sufficient to bring any catalytic transformation.

#### 4. Conclusion

In this study, waste generated during the educational process was used as a catalyst to promote circular economy, and sustainable waste management practice in academic laboratories. Cu<sub>2</sub>O was isolated as a second cycle waste, which was generated during the practical session (undergraduate laboratory course), where students used an aqueous

solution of recycled  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as a Fehling's reagent A. Isolated  $\text{Cu}_2\text{O}$  was characterized by IR, PXRD, XPS, SEM, and TEM. This waste-derived material was successfully used as an active catalyst for synthesizing a variety of  $\beta$ -keto-1,2,3-triazole in an aqueous medium with good to excellent yields. The catalytic performance of the second-cycle waste- $\text{Cu}_2\text{O}$  was found to be similar to that of first-cycle waste- $\text{Cu}_2\text{O}$  and commercial  $\text{Cu}_2\text{O}$ . The catalyst was reused for two consecutive catalytic cycles without significant product yield loss. The synthesized  $\beta$ -keto-1,2,3-triazole was also found to show a chelating property. Combining the bioactivity and chelating properties of  $\beta$ -keto-1,2,3-triazoles with copper opens up an opportunity for a supramolecular chemist, medicinal chemist, material chemist, and many.

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## CRediT authorship contribution statement

**Randhir Rai:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

## Declaration of Competing Interest

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.sceenv.2024.100205](https://doi.org/10.1016/j.sceenv.2024.100205).

## Data availability

Data will be made available on request.

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