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Wastewater treatment using waste cuprous oxide: A circular economy approach towards green and sustainable laboratory waste management

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ABSTRACT

In this study, waste Cu_2O was used as a Fenton-like catalyst for treating laboratory wastewater using hydrogen peroxide (H_2O_2) as an oxidant. The catalytic efficiency of Cu_2O towards the decomposition of crystal violet, methylene blue, and safranin was evaluated. The catalyst was recycled and reused up to five catalytic cycles without significant loss of catalytic efficiency against these dyes. Wastewater from the biology laboratory containing these toxic dyes was successfully treated using the same catalyst with excellent efficiency. Post-treatment, copper was recovered as copper sulphate pentahydrate with a 96 % of copper recovery. Furthermore, the toxicity of untreated and treated water was studied against *E. coli*. Additionally, the survival of the aerial microbes in treated water was evaluated and compared with that of drinking water, and it was found to be almost the same.

1. Introduction

The generation of wastewater is part of our daily life activities. Industries such as textiles, cosmetics, food processing, plastic, and rubber are the major sources of water pollution. It is well known that these industries discharge large amounts of dyes-contaminated wastewater. More than 100,000 organic synthetic dyes are available commercially, and more than 7×10^5 tons are produced annually and used by these industries [1]. These synthetic dyes can be categorized as either cationic (malachite green, crystal violet, methylene blue, etc) or anionic dyes (remazol brilliant blue R, congo red, methyl orange, etc) [2]. It is one of the most menacing organic contaminants discharged into water bodies [3]. It is highly toxic to aquatic and terrestrial ecosystems [4–6], and has been a serious issue in the last few decades. To reduce the toxicity of dyes contaminated wastewater on the environment, globally, researchers have conducted intense research to develop different methods for treating dyes contaminated wastewater or effluents [1]. Different known methods for wastewater treatment are the following: physical methods (adsorption, coagulation, membrane separation, and ion exchange) [7–10], chemical methods (oxidative degradation, reductive degradation, electrochemical treatments, and photochemical treatment) [11,12], biological methods (micro-organism) [13], and hybrid methods (physical/chemical, chemical/biological, and chemical/chemical) [1, 14,15]. In chemical treatments, oxidative and reductive decomposition are the two methods used generally for dye decomposition in wastewater. In oxidative methods, the organic contaminants are oxidized to non-toxic or less toxic smaller components via oxidation by making use of an oxidizing agent in the presence of a suitable catalyst [1, 5]. In reductive methods, mostly azo dyes (anionic dyes: methyl orange, congo red, metalin yellow, etc) are decomposed to corresponding amine components using reducing agents such as sodium borohydride, in the presence of a suitable catalyst [16] or by electrolytic reduction methods [17]. Chemical treatment (where contaminants get eliminated or decomposed to the smallest possible non-toxic or less toxic fragments) has an added advantage over physical methods. In the case of physical methods, the separated pollutants needed to be stored carefully following established guidelines, as there is always a risk of recontamination of the environment.

Catalytic oxidative decomposition of organic contaminants in wastewater are Fenton and Fenton-like processes [11,12,18,19]. The classic Fenton oxidation process has some disadvantages, including the requirements of a low pH (~ 3). At pH ≤ 2.5, excess of Fe^{3+} ions causes the rapid decomposition of H_2O_2 and formation of oxygen gas, which reduces the net amount of $^{\cdot}OH$ involved in the decomposition of contaminants. At pH > 4, due to the formation of ferric hydroxide, $Fe(OH)_3$, the appropriate amount of $^{\cdot}OH$ is not formed, making the process inefficient [20]. Many researchers have developed other transition metal-based Fenton-like catalysts to overcome such limitations for efficient wastewater treatment. Fenton-like catalysts are metal-based catalysts other than iron, such as copper (Cu), Cobalt (Co), Manganese

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(Mn), nickel (Ni), Zinc (Zn), Silver (Ag), and others [18]. We know that a large amount of resources are consumed to develop efficient catalysts for wastewater treatments. Therefore, to conserve resources, exploring the possible use of metal-based waste-derived materials in diverse fields is a essential step towards sustainable waste management and a circular economy. Recovery and upcycling add value to the economy and diminish its toxic effect on the environment. Among all these metals, copper needs special attention because copper scarcity is expected between the year 2039 and 2054 [21]. Hence, recovering copper from all possible waste sources is extremely important to maintain a demand-supply chain. Several reports exist in the literature on copper recovery or upcycling from electronic waste [22–24], and industrial wastewater [25–27]. However, the upcycling of copper-based laboratory waste started recently only [28,29].

As far as copper-based waste from academic laboratories is concerned, in most cases it is generated from well-known century-old reactions such as Fehling's reaction [30], Barfoed's reaction [31], and Benedict's reaction [32]. In each of these reactions, the product is cuprous oxide (Cu_2O), which is generally discarded as waste. Due to its diverse functional properties, the same waste Cu_2O can be considered as a critical resource. Cu_2O is a p-type semiconductor with a band gap of 1.9–2.2 eV and is widely used in solar energy conversion [33]. It also holds excellent antimicrobial properties and is used as an antimicrobial agent [34]. It has been reported that Cu_2O acts as a germ-fighting agent at the air-water interface to prevent potable water from aerial microbial contamination [35]. In organic synthesis, it serves as a highly efficient click-catalyst for the synthesis of 1,2,3-triazole [28,29,36–38] and in many other organic transformations [39]. In the advanced oxidation process of wastewater treatment, Cu_2O, (and other Cu-based materials) as Fenton-like catalysts is well established [40–51]. Therefore, the isolation of Cu_2O from waste and its application in wastewater treatment will promote green, economical, and sustainable development, which could lead to a circular economy.

In research and academic laboratories, dyes contaminated wastewater is also produced in significantly large quantities, specifically during practical classes and other research activities [52]. Commonly used dyes in academic laboratories include crystal violet, safranin, methylene blue, coomassie blue, phenolphthalein, methyl orange, etc. Biology students commonly use crystal violet, methylene blue, and safranin during practical sessions in various cell staining experiments, while methyl orange and phenolphthalein are mainly used as indicators in acid-base titration. Treatments of this wastewater using copper-based waste as a catalyst will help us move toward the direction of sustainable waste management. Such small steps will also help us in developing a circular economy practice in academia. Additionally, accepting copper-based waste as a resource will contribute to copper recycling [53] and prevention of copper toxicity in the environment [54].

In this study, we report Fenton-like catalytic activities of Cu_2O which was isolated from the laboratory waste. It was also employed as an active catalyst to treat dye-contaminated laboratory wastewater by using H_2O_2 as an oxidant. Post-water treatment, copper was recovered as $CuSO_4{\cdot}5\ H_2O$. Survival of aerial microbes in treated water and drinking water was compared.

2. Material and methods

2.1. Materials

Cu_2O was recovered from laboratory waste by separating it at the source [28]. Dyes, crystal violet, methylene blue, and safranin were purchased from Loba Chemie Pvt. Ltd., India Concentrated H_2SO_4 and 30 % H_2O_2 were obtained from Fischer Scientific, India. Agar and nutrient broth were purchased from Hi Media, India. Terephthalic acid was obtained from Sigma Aldrich, India.

2.2. Characterization

IR spectrum of Cu_2O was recorded by FT/IR-6X FTIR Spectrometer. XPS data were obtained from X-ray photoelectron spectrometer (SPECS, Germany). Absorbance and UV–visible spectra were recorded using a UV-3200 spectrophotometer (Lab India). SEM images of Cu_2O powder were recorded using FEI Quanta 200 Scanning electron microscope. Powder X-ray diffraction (PXRD) was obtained from a Bruker D8 Avance instrument with Cu Kα ($\lambda = 1.5406$ Å) radiation in reflection mode. Copper leaching was studied using an ICP-OES spectrometer. Fluromax Spectrofluorometer (Horiba Scientific) was used for the fluorescent measurement of 2-hydroxy terephthalic acid, in the hydroxyl radical detection experiment.

2.3. Isolation of Cu_2O from laboratory waste

Cu_2O-waste was generated during the practical session where undergraduate students were tasked with estimating the quantity of reducing sugar using Fehling's solution titration method [28]. A detailed experimental procedure for quantitatively estimating and reducing sugar is described in the Supporting information. After each titration experiment, the students were asked to transfer the reaction mixture into separate waste-collecting containers. After the class, we separated Cu_2O by simple filtration using Whatman filter paper. Filtered Cu_2O was washed three times with water (3 ×10 mL), and air-dried. We obtained 12–15 g of Cu_2O per batch of students.

2.4. General procedure for dye decomposition

In a typical dye degradation experiment, 10 mg Cu_2O catalyst powder was taken in a 100 mL beaker and 100 mL of 0.1 mM aqueous dye solution was added to it. The reaction mixture was kept on a thermostatic magnetic stirrer and heated to 50 ℃ with continuous stirring. At the same temperature, 1 mL of 30 % aqueous solution of H_2O_2 was added. Further, at different time intervals, 0.3 mL of the reaction mixture was taken in a quartz cuvette and 2.7 mL of water was added to it. The absorbance was measured using UV-Vis spectrophotometer. For crystal violet, the absorbance was measured at 590 nm at a time interval of 10 min and complete dye decomposition was observed at 30 min. For methylene blue and safranin, the absorbance was measured at 663 nm and 520 nm at a time interval of 1 hour. The complete decomposition time for methylene blue and safranin was found to be 6 h and 10 h, respectively. Another batch of experiments was performed without a catalyst by keeping all other reaction parameters the same. For each dye, the degradation reaction was triplicated with and without a catalyst.

2.5. Terephthalic acid fluorescence probe

It is known that terephthalic acid (TA) undergoes hydroxylation in the presence of hydroxyl radical (·OH) and gets converted to 2-hydroxy terephthalic acid (TA-OH), which emits fluorescence at 426 nm on excitation at 310 nm [55]. 100 mL of 1 mM of TA stock solution was prepared by dissolving 1.6 mg of TA in water, and the pH of the solution was brought to 11.5 by adding 0.1 M NaOH solution dropwise. 10 mL of the TA stock solution was taken and one drop of H_2O_2 (30 %) was added to it. The fluorescence was recorded within one minute, and low-intensity fluorescence was observed at 426 nm. In another batch, 10 mL of TA stock solution was taken in a beaker containing 0.5 mg Cu_2O and kept in a magnetic stirrer. One drop of 30 % H_2O_2 was added to the reaction mixture, and within one minute, fluorescence was measured. We observed significantly intense fluorescence at 426 nm which is due to the formation of TA-OH.

2.6. Recyclability of catalyst

Prior to the recyclability test, a fresh batch of catalytic reactions was carried out, as mentioned in the previous section. After the first run, the reaction mixture was first kept aside for around 2 h. Once the catalyst settled at the bottom of the beaker, the fluid was decanted slowly and the catalyst was recovered for the next run. 100 mL of 0.1 mM dye solution was added to the beaker containing the recovered catalyst and heated on a thermostatic magnetic stirrer with continuous stirring. Once the temperature reached 50 °C, 1 mL of 30 % H_2O_2 was added to it, and absorbance was measured at the beginning and end of the reaction. The reaction time for crystal violet, methylene blue, and safranin was fixed at 0.5, 6, and 10 h, respectively. The catalyst was recycled and reused against each dye degradation reaction up to five catalytic cycles without significant loss of catalytic activity.

2.7. Laboratory wastewater treatment

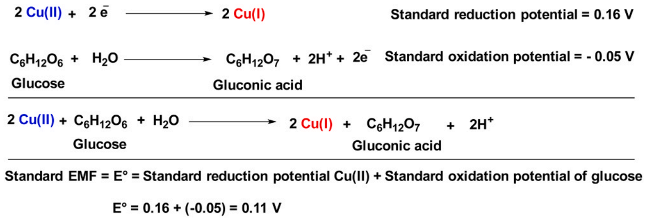
Laboratory wastewater was collected from the biology laboratory where crystal violet, methylene blue, and safranin contaminated wastewater was generated by undergraduate students during their practical session (detailed experimental procedures are described in Supporting information). The wastewater also contains small amount of ethyl alcohol and acetone as other organic contaminants. 2 g of Cu_2O catalyst and 2 Liter of laboratory wastewater was taken in a crystallization dish and kept on a thermostatic magnetic stirrer and heated to 50 °C. Following this, 10 mL of 30 % H_2O_2 was added and the mixture was continuously stirred. At different time intervals, 1.5 mL of the reaction mixture was taken in a quartz cuvette and diluted two-fold by adding 1.5 mL of water to it. The UV–visible absorption spectra were recorded, to monitor the progress of the reaction. After 12 h another 10 mL of 30 % H_2O_2 was added. After a total reaction time of 24 h, the reaction mixture turned almost colorless, and in UV–visible spectra, no absorption peak corresponding to any of these dyes was observed.

2.8. Recovery of copper from treated wastewater

As mentioned in Section 2.6, the laboratory wastewater was completely decolorized after a reaction time of 24 h. Following this, the reaction mixture continued stirring for another 24 h. The color of the mixture turned light blue due to the oxidation of Cu(I) to Cu(II), resulting in the formation of an aqueous solution of Cu^{2+} ions. 10 mL of 2 M NaOH solution was added dropwise to the reaction mixture, and precipitation of $Cu(OH)_2$ was slowly observed. After the complete precipitation of $Cu(OH)_2$, the mixture was filtered using Whatman filter paper, and $Cu(OH)_2$ was separated. Filtered treated water was kept in a reagent bottle for further study. $Cu(OH)_2$ was air-dried and a weight of 2.67 g (27.36 mmol) was obtained. $Cu(OH)_2$ was transferred to 100 mL beaker, and 20 mL of 2 M H_2SO_4 was added to it dropwise, and blue color copper sulphate solution was obtained. Copper sulphate pentahydrate was crystallized by slow evaporation of the solvent in a hot water bath at 95 °C. The weight of the isolated $CuSO_4 \cdot 5H_2O$ was found to be 6.7 g (96 % copper recovery).

2.9. Toxicity study of untreated wastewater against E. coli

Three 250 mL conical flasks were taken (I-III), 100 mL of tap water was added to each, and the mouth of each flask was closed with cotton plugs. Each of these flasks with water was sterilized by autoclaving at 121 °C for 15 min and cooled down to room temperature. Each flask containing 100 mL sterile water was contaminated with 0.1 mL of freshly cultured *E. coli* (~ 10^5 CFU/mL). To flask I, 1 mL of drinking water was added. To flasks II and -III, 1 mL of untreated and treated water was added respectively and kept in a rotary incubator shaker at 37 °C at 150 rpm. At a time interval of 2 h, 0.1 mL of each water sample was inoculated on a nutrient agar plate and incubated at 37 °C for 24 h. Variations in CFU/mL in each water sample were analyzed via the serial dilution method. A total of 0.1 mL of each water sample was taken in plastic hinge-top vials, and 10-fold serial dilutions were performed. A total of 0.1 mL of each diluted water sample was inoculated on a nutrient agar plate and incubated at 37 °C for 24 h, and CFU/mL was counted. After 6 h, the microbial contamination in the water sample where 1 mL of untreated water was added, was found to be below the detectable limit. Whereas the bacterial population in the water sample where 1 mL of drinking water and the treated water were added was found to be almost similar.



$$2\,Cu(II) + 2\bar{e} \longrightarrow 2\,Cu(I) \qquad \text{Standard reduction potential = 0.16 V}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + H_2O \longrightarrow \underset{\text{Gluconic acid}}{C_6H_{12}O_7} + 2H^+ + 2\bar{e} \qquad \text{Standard oxidation potential = - 0.05 V}$$

$$2\,Cu(II) + \underset{\text{Glucose}}{C_6H_{12}O_6} + H_2O \longrightarrow 2\,Cu(I) + \underset{\text{Gluconic acid}}{C_6H_{12}O_7} + 2H^+$$

Standard EMF = E° = Standard reduction potential Cu(II) + Standard oxidation potential of glucose

$E° = 0.16 + (-0.05) = 0.11$ V

Scheme 1. Redox reaction between Cu(II) and glucose (reducing sugar).

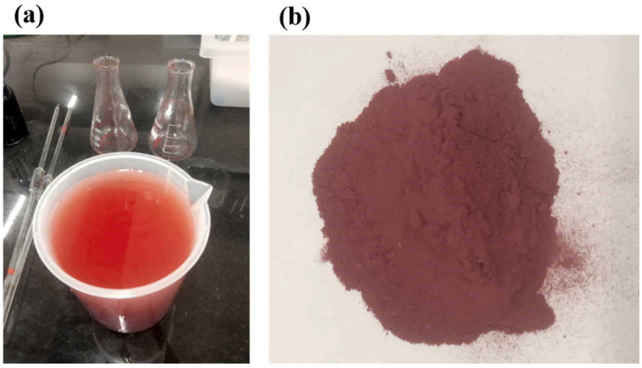


Fig. 1. Images showing (a) copper-based waste generated in the chemistry laboratory by undergraduate students after experimenting, “Quantitative estimation of reducing sugar using Fehling’s reaction” and (b) Isolated Cu_2O powder.

2.10. Aerial microbe survival in treated water

Two 250 mL beakers were taken. In one beaker, 200 mL of drinking water was added, and in the other beaker, 200 mL of treated water was added. Both beakers were kept outside the laboratory premises in the building for 3 days. At a time interval of 24 h, 0.1 mL of water from each sample was poured into agar nutrient and spread uniformly with a sterile L-rod. Three agar nutrient plates were inoculated for each water sample. The inoculated plates were incubated at 37 °C for 24 h, and depending upon the microbial contamination in the water sample, the intensity of microbial growth was observed. Variation in CFU/mL was analyzed *via* serial dilution methods as described in the previous section.

3. Results and discussion

3.1. Copper-based waste

In the category of inorganic waste, copper-based waste is of utmost importance. In academic laboratories, specifically at the School of Chemical Science, copper-based waste is generated in large quantities during the practical session [28]. The most commonly used copper-based reagent in academia is Fehling’s reagent, alkaline copper-tartrate complex. This reagent is used for qualitative and quantitative estimation of reducing sugar. The standard redox potential of gluconic acid to glucose and Cu(II) to Cu(I) is 0.05 V and 0.16 V respectively and the E°_{cell} for production of Cu_2O is 0.11 V, which facilitates the redox reaction (Scheme 1) [56]. Most commonly in

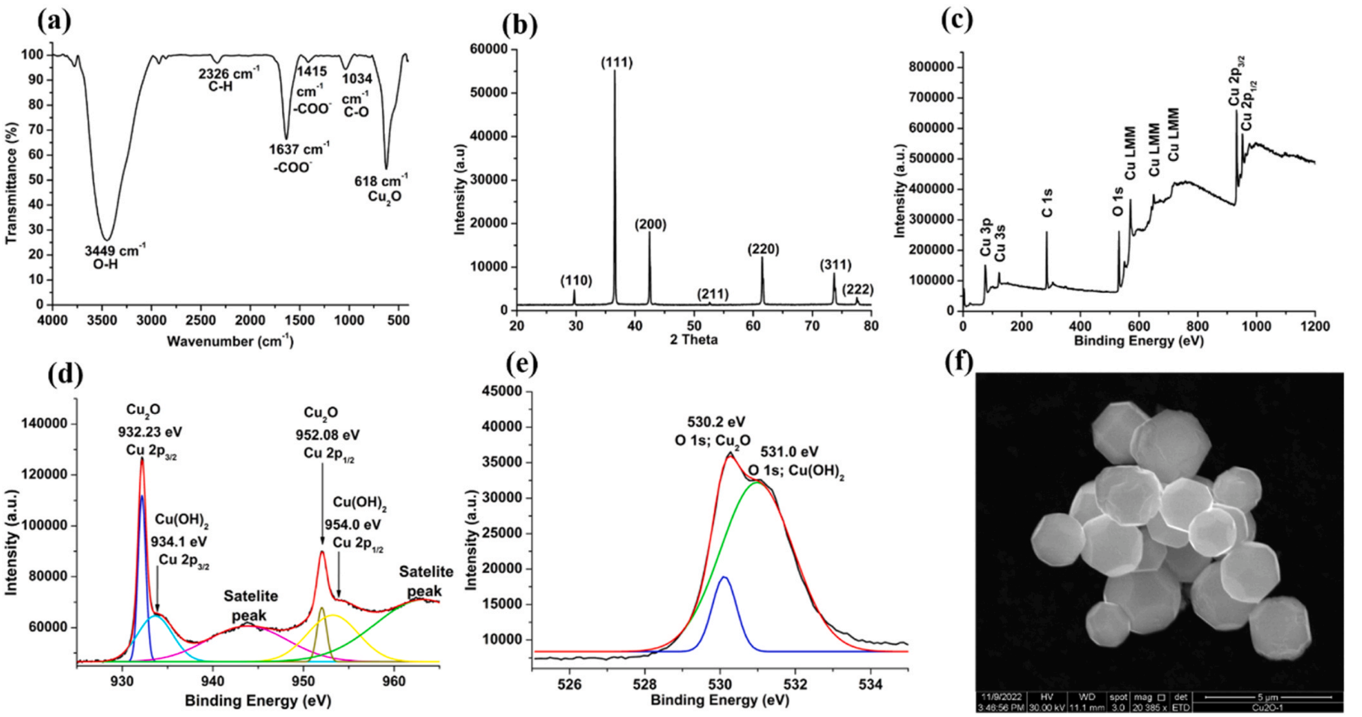


Fig. 2. (a) FT-IR spectrum of the recovered Cu_2O, (b) PXRD of Cu_2O, (c) XPS survey spectrum, (d) XPS high-resolution Cu 2p spectrum, (e) XPS high-resolution O 1s spectrum, and (f) SEM image of Cu_2O.

academic laboratories, the formed Cu_2O is discarded as a hazardous transition metal-based waste. Similar waste was generated in our chemistry laboratory by our undergraduate students where they were assigned to estimate quantitatively the amount of reducing sugar in a given sample (Fig. 1). During the recovery of copper from the waste, if a small quantity of copper may get discharged into the environment, which can act as a micronutrient to plants and other species [57,58]. At the same time, when contamination of copper in the environment increases beyond a certain limit, it becomes toxic [54,59]. The toxic effect of copper on the environment can be prevented only by its recovery from the waste. Looking at the environmental aspect, and diverse application of copper-based materials, we extended our previous work [28] and used waste Cu_2O as an active Fenton-like catalyst for wastewater treatment. Such an approach will not only help in recycling material but also help us build a new concept towards waste management, “Waste for Waste-treatments” which will also strengthen the circular economy.

3.2. *Characterization of Cu_2O*

In the IR spectrum of isolated Cu_2O (Fig. 2a), a peak at 618 cm^{-1} is due to Cu-O stretching [28,29]. Other peaks (1034, 1415, 1637, 2326, and 3449 cm^{-1}) correspond to physisorbed or chemisorbed tartarated from Fehling’s reagent B and gluconate, an oxidized product of glucose. A peak at 1034 cm^{-1} corresponds to C-O stretching. Symmetric and asymmetric vibration of carboxylate (-COO) ion peaks are observed at 1415 cm^{-1} and 1637 cm^{-1} respectively. C-H stretching was observed at 2326 cm^{-1} and that of O-H and adsorbed at 3449 cm^{-1}. Powder X-ray diffraction (PXRD) spectrum of Cu_2O shows the entire characteristic Bragg’s reflection at appropriate 2θ, (110), (111), (200), (211), (220), (311) and (222) miller plane which corresponds to Cu_2O (Fig. 2b). The obtained PXRD results are consistent with the values in the standard Joint Committee on Powder Diffraction Standards (JCPDS No. 05-0667) [28,29,37,38]. The oxidation state of Cu and other Cu-impurities in the sample was analyzed by X-ray photoelectron spectroscopy (XPS). In the survey scan, binding energy peaks were found at 283, 530, and 933 eV corresponding to Carbon (C 1s), oxygen (O 1s), and copper (Cu 2p), respectively (Fig. 2c). Intense peaks at 932.23 and 952.08 eV correspond to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ respectively (Fig. 2d), the characteristic feature of the Cu(I) ion. Additionally, binding energy peaks at 934.1 and 954.0 eV corresponded to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ respectively of Cu(II) ions were also observed. The core level peak of O 1s was observed at 530.2 eV and 531.0 eV is the characteristic feature of the oxygen of Cu_2O and $Cu(OH)_2$ respectively (Fig. 2e). The binding energy information confirmed that the sample was Cu_2O and a small amount of Cu $(OH)_2$ as impurities and the results are in good agreement with the data available in the literature [28,29 60]. In the SEM image, the particle size is 1–4 μm (Fig. 2f).

Table 1
Upcycling of copper-based Fenton-like catalyst from different waste source.

Source	Cu-based materials	Catalytic application against organic contaminants	Ref.
Simulated Cu(II) waste effluents	CuO nanosheet	Phenol	[61]
Electronic waste	CuNPs	surfactant	[62]
Electronic waste	Cu-coated carbon	Rhodamine B	[63]
Electronic waste	CuO/Cu_2O	Nitrophenol	[64]
Laboratory waste	**Cu_2O**	**Crystal violet, Methylene blue, Safranin, and Laboratory wastewater**	**This work**

3.3. *Fenton-like activity of waste Cu_2O*

Many researchers have developed copper-based Fenton-like catalysts for efficient wastewater treatment (Table S1) [40–51]. At the same time, a few research groups have reported the recovery of copper and copper-based materials from different waste sources and their applications in water treatment (Table 1). Fang et al., recovered copper as CuO from simulated Cu(II) waste effluents and used it as a Fenton-like catalyst to decompose phenol in water [61]. Martins and group synthesized Cu-nanoparticles (CuNPs) from electronic waste and studied its

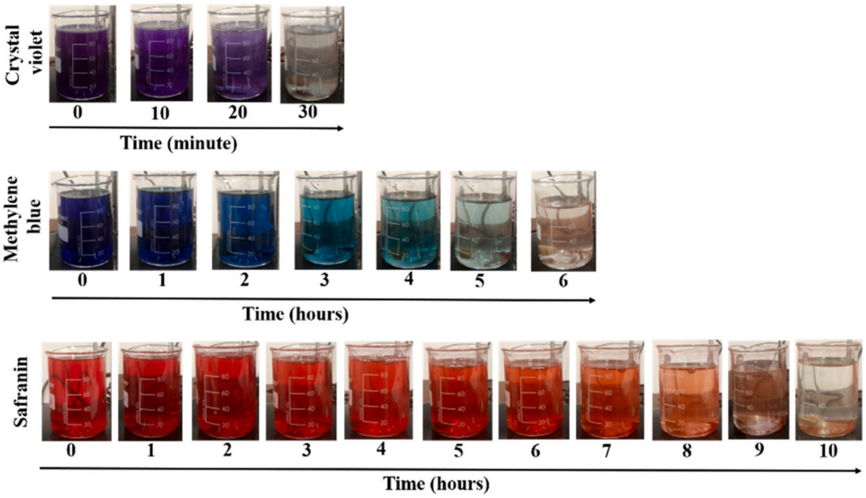


Fig. 3. Images showing the decrease in color intensity of dye decomposition reaction mixture with time.

catalytic potential towards the degradation of mining surfactant [62]. Similarly, a few more researchers reported the upcycling of Fenton-like copper-based catalysts from electronic waste [63,64]. We too accepted waste as a wealth and studied the Fenton-like activity of waste Cu_2O towards the decomposition of crystal violet, methylene blue, and safranin. This waste material was applied to treat real laboratory wastewater contaminated with these dyes.

Treatment of 100 mL of a 0.1 mM aqueous crystal violet solution with 1 mL of 30 % aqueous H_2O_2 in the presence of 10 mg of Cu_2O at 50 ℃ at neutral pH took 30 min for complete decoloration (Fig. 3). Under the same reaction condition methylene blue and safranin took 6 h and 10 h respectively for complete decoloration (Fig. 3). In the crystal violet decomposition experiment, at time intervals of 10 min 0.3 mL of the reaction mixture was taken in a quartz cuvette and diluted 10 times by adding 2.7 mL of water, and absorbance at 590 nm was recorded (Table S2). For methylene blue and safranin, the absorbance was measured at 663 nm and 520 nm respectively at a time interval of 1 hour (Table S3 and S4). The absorption spectra of the decomposition of dyes at different time intervals and the comparison of catalyst performance are described in Fig. 4. Further, the mineralization dyes were also analyzed through chemical oxygen demand (COD) measurement (detailed experimental procedure is provided in Supporting information). The method used in this study was the standard potassium dichromate method. At time zero the COD of crystal violet, methylene blue, and safranin solution was found to be 93.33 ± 2.30, 78.66 ± 2.30, and 86.66 ± 2.30 respectively (Tables S5–S7). After complete decolorization of the dyes, their respective COD was found to be 24, 14.66 ± 2.30, and 24 respectively (Tables S5–S7). After complete mineralization, the percentage of COD removal for crystal violet, methylene blue, and safranin was found to be 74.27 ± 0.62, 81.40 ± 2.43, and 72.28 ± 0.74 percent respectively (Fig. 4j–l.)

The recyclability of the catalyst was performed using crystal violet, methylene blue, and safranin as a model substrate. The experiments were performed as described in previous dye decomposition test experiments. After the first round of the catalytic decomposition cycle, the reaction mixture was kept aside for 2 h to settle down the catalyst at the bottom of the beaker (Fig. 5). Then the fluid was decanted slowly and 100 mL of 0.1 mM dye solution was added and heated up to 50 ℃. Following this, 1 mL of 30 % H_2O_2 aqueous solution was added to it and continuously stirred till it was complexly decolorized. Absorbance at 590 nm, was measured for crystal violet at the beginning and after 30 min of reaction time (Table S8). For methylene blue and safranin, the absorbance was measured at 663 nm, and 520 nm respectively. End reaction times for methylene blue and safranin were taken as 6 h and 10 h for every cycle.

A fresh set of experiments were conducted to analyze the copper leaching into the water during the demineralization of these dyes. After completion of each reaction cycle, water was transferred to a centrifuge tube and centrifuged at 5000 rpm for 30 min to separate the dispersed Cu_2O particles from the treated water completely, and the supernatant was analyzed through ICO-OES analysis. The copper leaching at each cycle was found to be around 1.5–3 mg/L with a catalyst dose of 0.1 g/L (Fig. 6, Table S9).

3.4. Possible mechanism involved in Fenton-like reaction by Cu_2O

Cu_2O is a well-known catalyst for generating hydroxyl radical ($^{\cdot}$OH) and hydroperoxyl radical (HOO$^{\cdot}$), which are a very strong oxidizing agent [48]. H_2O_2 after getting adsorbed on the surface of Cu_2O surface, Cu(I) gets oxidized to CuO, and $^{\cdot}$OH radical and hydroxyl anion ($^{-}$OH) are produced. Few reports in the literature claim that terephthalic acid (TA) in the presence of $^{\cdot}$OH radical undergoes hydroxylation and results in the formation of 2-hydroxy terephthalic acid (TA-OH) (Scheme 2) which emits fluorescence at 426 nm when excited at 310 nm [55]. To confirm the formation of $^{\cdot}$OH radical in our Fenton-like catalytic activity, after the addition of one drop of H_2O_2 to the TA solution containing Cu_2O particles, within a minute intense fluorescence was observed at 426 nm when excited at 310 nm (Fig. 7). When one drop of H_2O_2 was added to TA solution in absence of Cu_2O particles, poor fluorescence was observed which may be due to self-decomposition of H_2O_2 to $^{\cdot}$OH radical and formation of TA-OH take place in low amount. No characteristic fluorescence was observed when only the TA solution was excited at 310 nm. This result confirmed that the Cu_2O is actively participating in the generation of $^{\cdot}$OH radical from H_2O_2.

Further H_2O_2 reacts with Cu(II) and produces HOO$^{\cdot}$ and proton (H^+) (Scheme 3). These in-situ generated strong oxidant ($^{\cdot}$OH and HOO$^{\cdot}$) oxidized dye molecules to carbon dioxide, water, and other possible smaller decomposed products. The formation of CuO was further confirmed by PXRD and XPS analysis of the catalyst recovered after the fifth cycle. During the copper leaching test experiment, all the used catalysts were isolated by centrifugation. Additionally, to obtain a sufficient amount of used catalyst for analysis, three batches of recyclability experiments were performed using each dye, and after each run the catalyst was separated by centrifugation at 5000 rpm for 30 min and air dried. The PXRD of this used catalyst shows all the characteristic Bragg's diffraction at appropriate 2θ corresponding to Cu_2O (Fig. 8a). Additionally, low-intensity peaks at 2θ of 35.5 and 38.7 2 were observed corresponding to (111) and (200) miller planes of CuO (Fig. 8b) [65]. A fresh batch of crystal violet was decomposed by making use of H_2O_2 as an oxidant in the presence of Cu_2O as a Fenton-like catalyst. After fifth

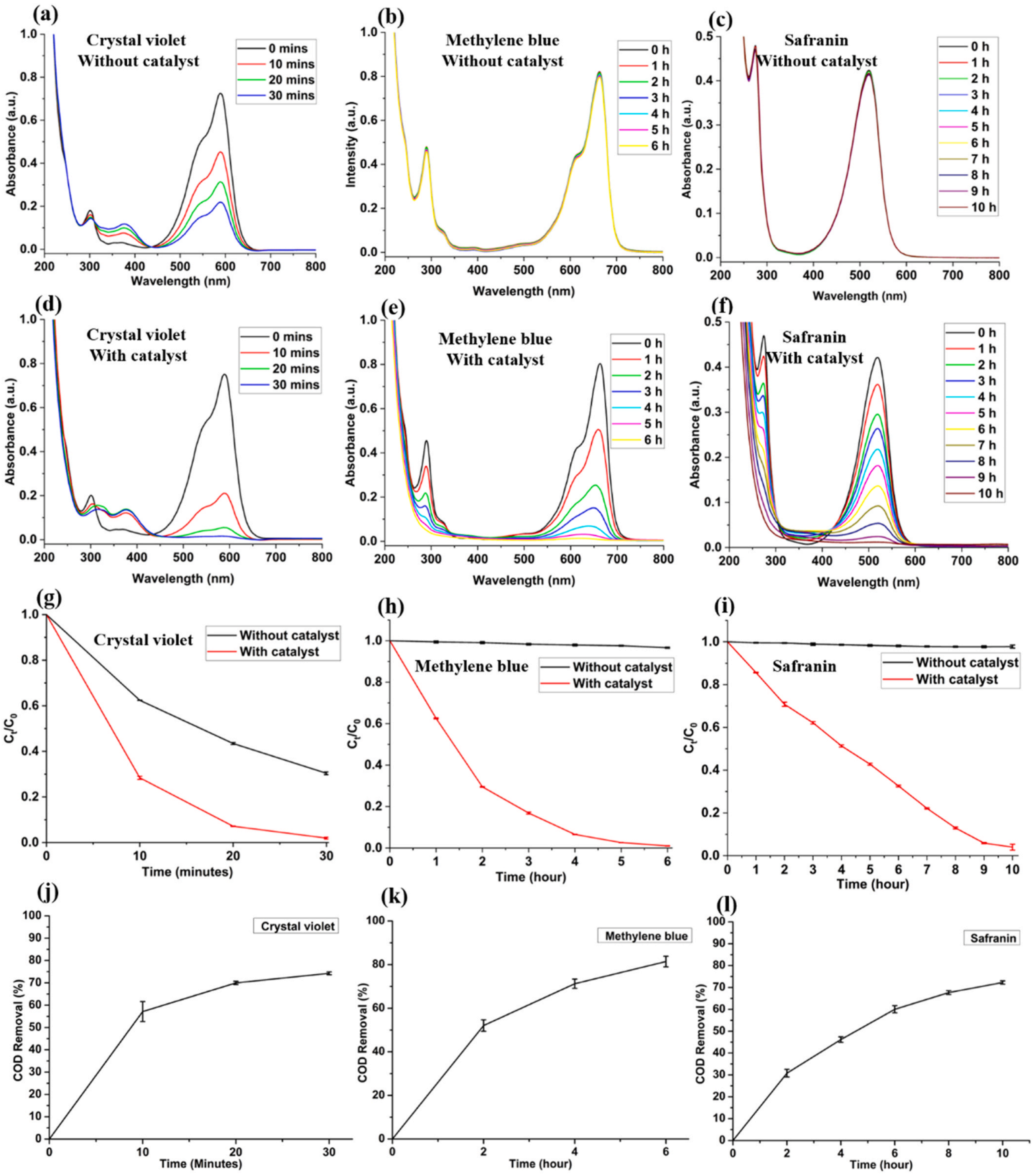


Fig. 4. UV-Vis spectra of dye decomposition without catalyst (a) crystal violet, (b) methylene blue, and (c) safranin. UV-Vis spectra of dye decomposition with catalyst (d) crystal violet, (e) methylene blue, and (f) safranin. Comparison of Cu_2O catalyst performance towards the decomposition of (g) crystal violet, (h) methylene blue, (i) safranin. Percentage of COD removal with time (j) crystal violet, (k) methylene blue, and (l) safranin.

cycle, the catalyst was separated by centrifugation at 5000 rpm at 25 ℃ for 10 min, and air dried. In the XPS spectra of the same sample, we observed characteristic features of Cu_2O, CuO, and $Cu(OH)_2$ (Fig. 8c-e). In the full survey scan spectrum, binding energy peaks around 282, 530, and 932 eV carbon (1s), oxygen (1s) and copper (2p) respectively were observed. Detection of intense peaks at 932.5 eV and 952.6 eV corresponds to $Cu2p_{3/2}$ and $Cu2p_{1/2}$ respectively. These peaks are almost the same as we observed in our previous report which corresponds to Cu(I) [28]. Additionally, low-intensity peaks at 934.6 eV and 954.1 eV were observed, indicating a Cu(II) in the sample, which is in close agreement with the literature [60]. In the core oxygen 1 s spectrum (Fig. 3c), its asymmetry was resolved using Gaussian fitting into three

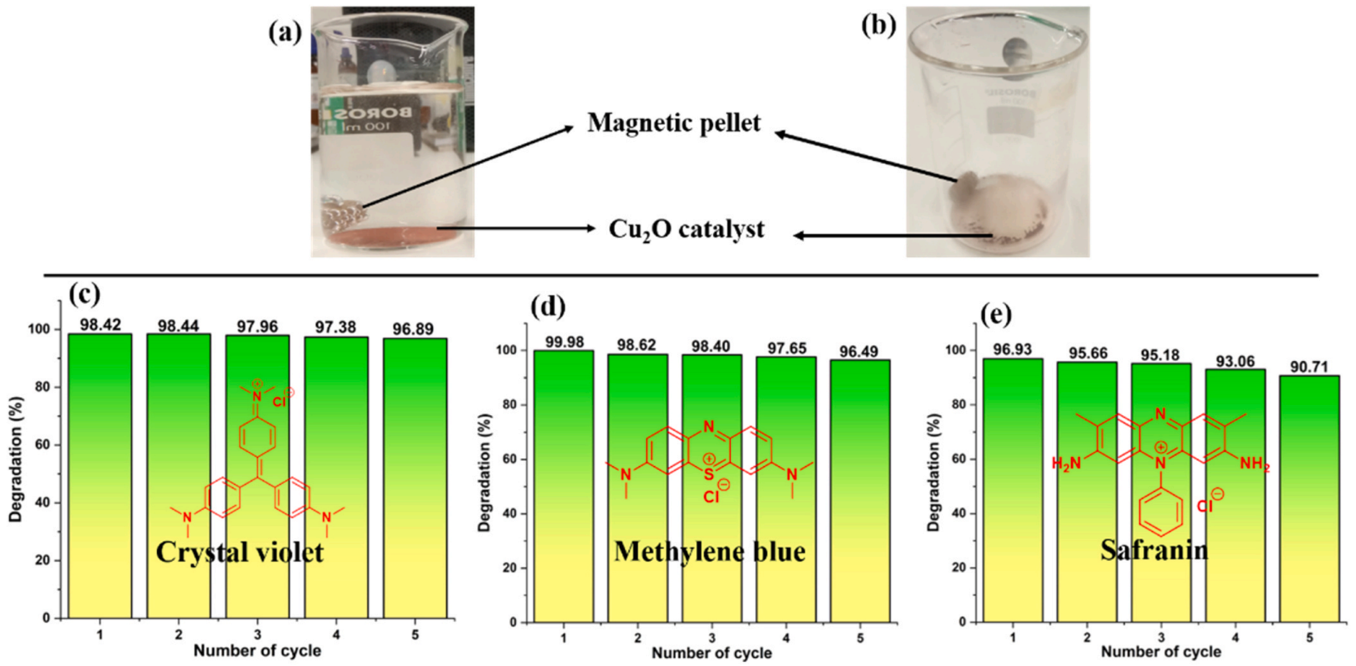


Fig. 5. (a) Image showing catalyst settled at the bottom of the beaker after standing for 2 h. (b) Recovered catalyst after decanting the fluid from the beaker for the next catalytic cycle. Cycling runs for the catalytic degradation of dye solution in the presence of the Cu_2O catalyst (c) crystal violet, (d) methylene blue, and (e) safranin.

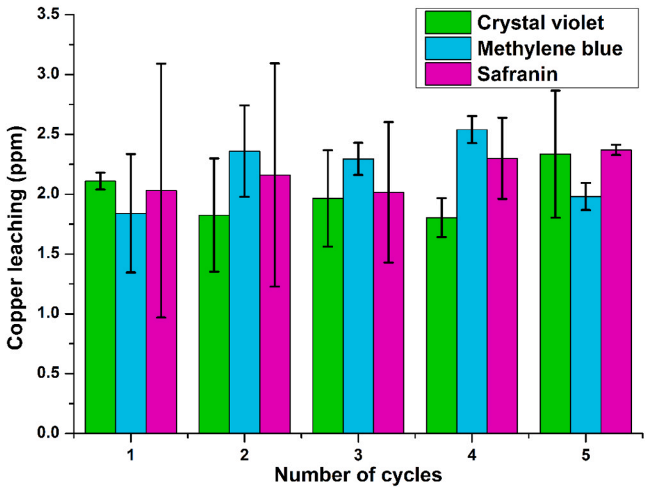


Fig. 6. Copper leaching after each catalytic cycle.

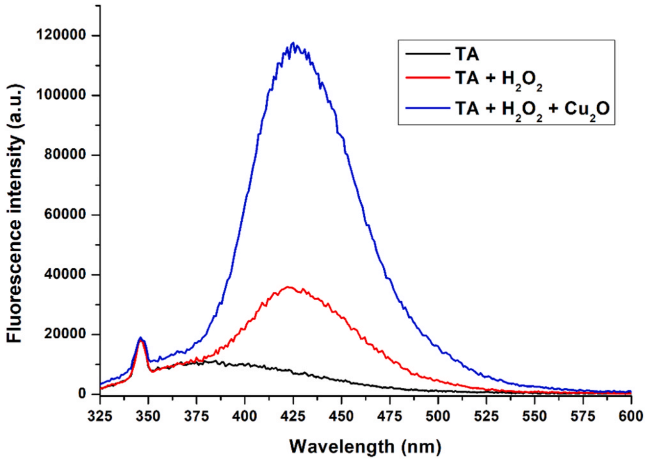
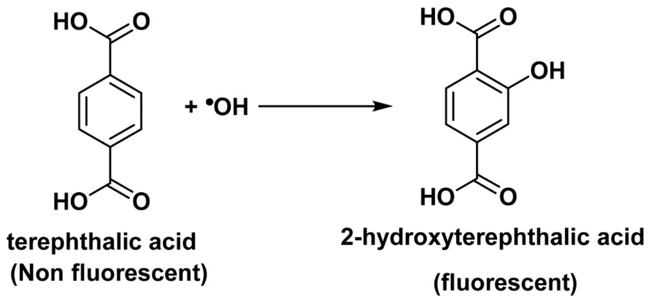
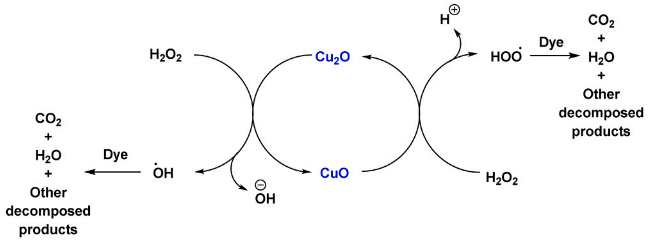


Fig. 7. Fluorescent spectra obtained after treatment of terephthalic acid with H_2O_2 and Cu_2O.



Scheme 2. Hydroxylation of terephthalic acid to 2-hydroxy terephthalic acid.



Scheme 3. Generation of ˙OH and HOO˙ radicals from Cu_2O and in-situ generated CuO.

separate curves, which is the indication of different chemical environments corresponding to lattice oxygen. The peak position values at 529.4 eV, 530.6 eV, and 531.3 eV correspond to CuO, Cu_2O, and Cu

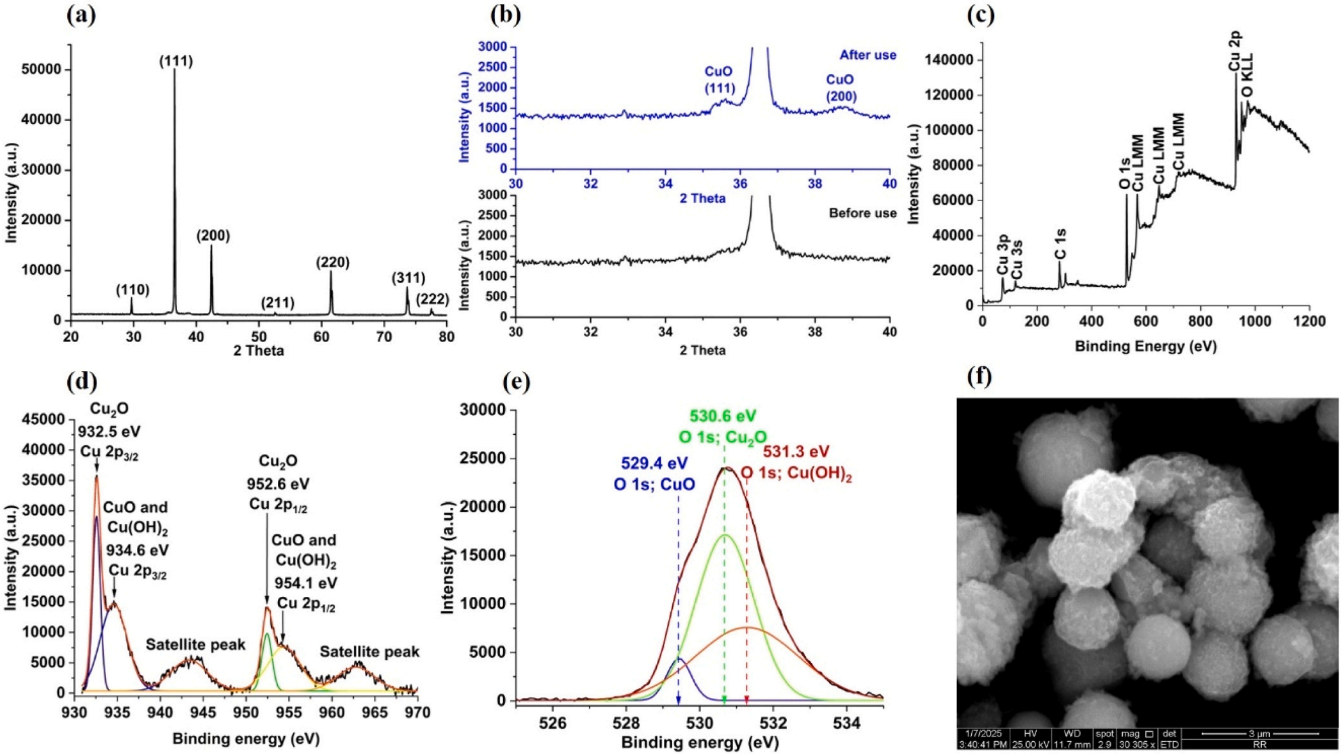


Fig. 8. (a) PXRD spectrum of the catalyst after fifth cycle. (b) Enlarged PXRD of the catalyst before and after use. XPS spectra of used Cu_2O catalyst after fifth cycle (c) Survey spectrum, (d) XPS high-resolution Cu 2p spectrum, and (e) XPS high-resolution O1s spectrum. (f) SEM image of Cu_2O-catalyst after the fifth catalytic reaction cycle against crystal violet decomposition.

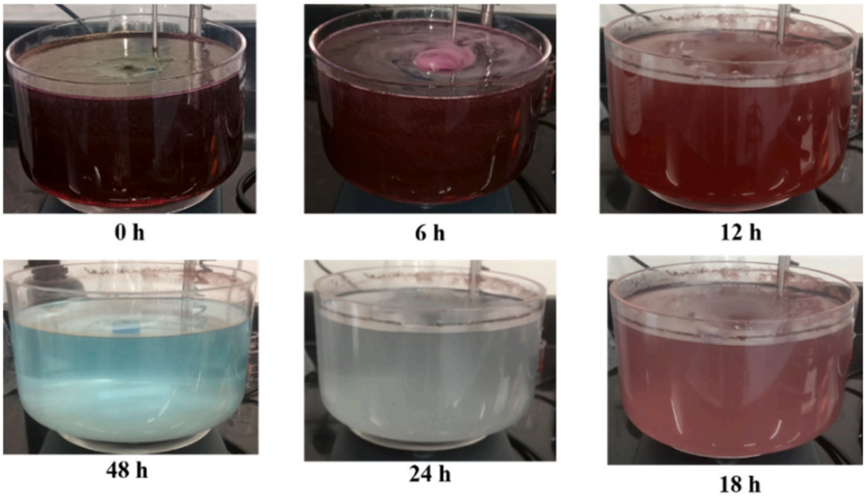

0 h
6 h
12 h
48 h
24 h
18 h

Fig. 9. Images showing laboratory wastewater treatment at different times.

$(OH)_2$ respectively which are also in close agreement with the data reported in the literature [28,66]. All these XPS analytical data confirm that during the Finton-like catalytic cycle, CuO forms (Scheme 3). In the SEM image, the morphology and surface texture of unused Cu_2O were polyhedral and very smooth (Fig. 2f). Whereas the surface texture of used Cu_2O after the fifth catalytic cycle was found to be rough and spherical (Fig. 8f). This roughness of the surface may be due to a change in its surface composition to CuO. The transformation of the morphology of the particles from polyhedral to spherical shape is probable due to stress caused by the ·OH radicles during the Finton-like process.

3.5. *Laboratory wastewater treatment and copper recovery*

Among transition metal-based Fenton-like catalysts, Copper-based Fenton-like catalysts were given special attention due to their economical availability and low toxicity. Many researchers have reported that copper-based Fenton-like catalysts can treat different wastewater (Table S1). Investment is required for the synthesis of catalysts in these methods. In the categories of waste, there is another type of waste called transition metal-based waste. The application of such waste as a catalyst for the treatment of wastewater will promote a circular economy as well as green and sustainable waste management.

Laboratory wastewater contaminated with crystal violet, methylene

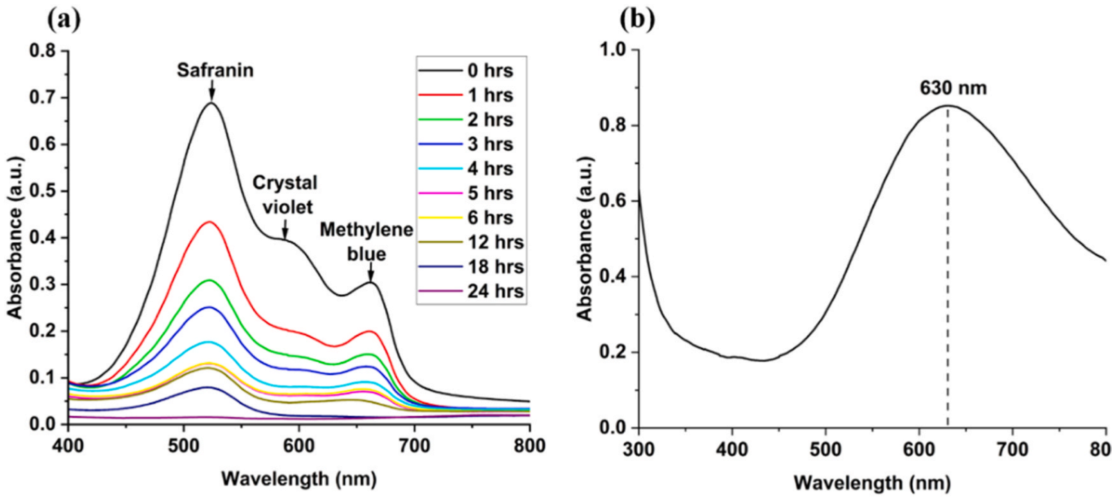


Fig. 10. (a) UV–visible absorption spectra of laboratory wastewater treatments at different time intervals. (b) UV–visible absorption spectra of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ coordination complex.

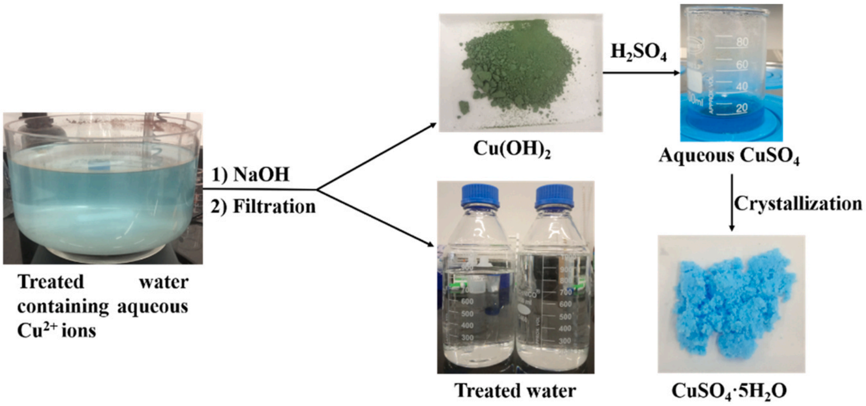
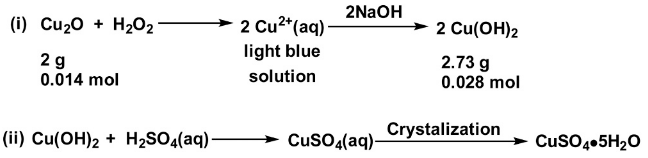


Fig. 11. Pictorial and schematic representation of copper recovery from treated wastewater.

blue, and safranin was collected from the biology laboratory, which was generated during a practical session where undergraduates were taught different cell staining methods (Fig. 9). 2 g of the catalyst was used against 2 Liters of wastewater. At 50 C, 10 mL of the 30 % H_2O_2 was added and continuously stirred. At a time interval of 1 hour, UV-Vis absorption spectra of the reaction mixture were recorded, and till 5 hours, a continuous decrease in the concentration of all three dyes in the reaction mixture was observed (Fig. 10a). The concentration of the dyes in the reaction mixture at the fifth hours and sixth hours was found to be almost the same, this may be due to consumption of a major fraction of H_2O_2. After this the reaction mixture was continuously stirred at the same temperature for the next six hours and at twelve hours, very small decrease in the concentration of the dyes was observed. Following this another 10 mL of 30 % H_2O_2 was added and at a time interval of 6 h UV-Vis absorption spectra were recorded and at 24 h complete decomposition of the dye contaminants was observed. Time taken for the decomposition of dyes in wastewater is more than that of the time taken by individual dyes. This may be due to the presence of other organic contaminants such as ethyl alcohol and acetone in the wastewater. Ethyl alcohol and acetone were used by our students during their practical classes for washing glass slides and watch glasses. The obtained organic waste was also discarded in the same container holding dyes contaminated wastewater. Possibly, ethyl alcohol and acetone act as a competitor towards the generated ·OH radicals and less amount of ·OH radicals are available for dye decomposition. To make sure all the H_2O_2 used in the reaction decomposed, the reaction mixture was continuously stirred for another 24 h and after 48 h of total reaction time, the color of the reaction mixture became light blue. This was due to the conversion of Cu_2O to aqueous Cu^{2+}. To confirm the conversion of Cu_2O to aqueous Cu (II), 1.5 mL of the solution was taken in a quartz cuvette and 1.5 mL of concentrated ammonia solution was added to it, and immediately deep blue color appeared due to the formation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ coordination complex. The formation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ coordination complex was further confirmed by recording UV–visible absorption spectra and the absorbance band at 630 nm was observed (Fig. 10b), which is in close agreement with the data reported in the literature [67].



Scheme 4. (i) Cu_2O leaching as aqueous Cu^{2+} and recovery as $Cu(OH)_2$ (0.028 mol, 2.73 g, theoretical yield). (ii) conversion of isolated $Cu(OH)_2$ to $CuSO_4·5H_2O$ (6.7 g, 96 %).

To recover the copper from treated wastewater, the reaction mixture was cooled down to room temperature and a solution of 2 M NaOH was added to it with continuous stirring to precipitate Cu^{2+} ions as copper hydroxide ($Cu(OH)_2$). Precipitated $Cu(OH)_2$ was filtered using Whatman filter paper and air-dried. The filtered water was stored in a reagent

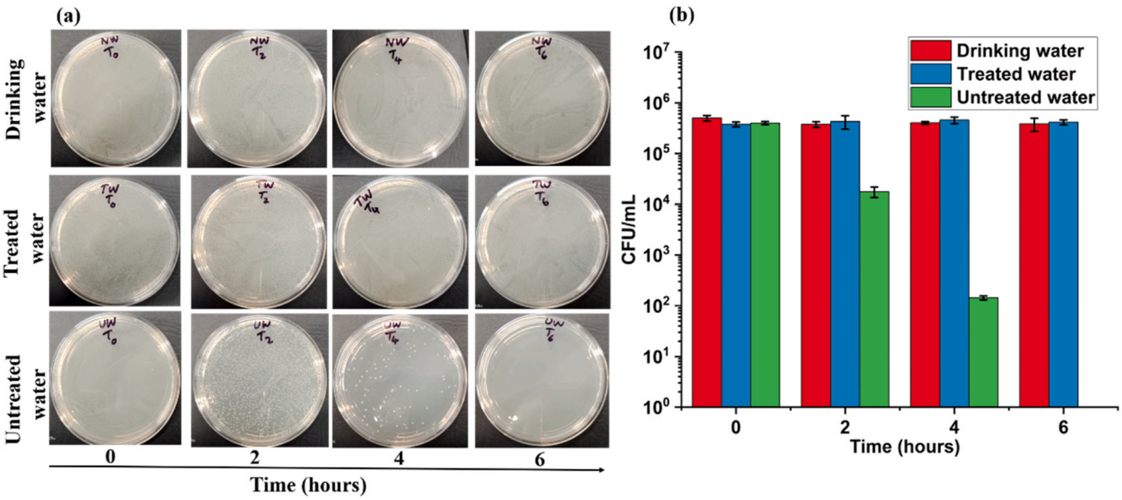


Fig. 12. (a) Nutrient agar plates showing bacterial population (*E. coli*) in 0.1 mL of each water sample at a time interval of 2 h. (b) Variation of CFU/mL with standard error bar.

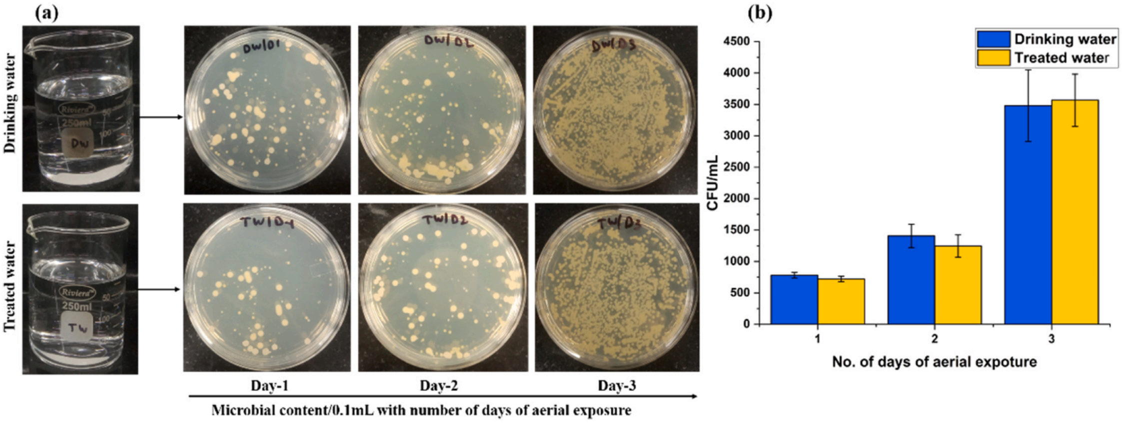


Fig. 13. (a) Nutrient agar plate showing microbial content in 0.1 mL of drinking water and treated water sample at a time interval of 24 h. (b) Variation of CFU/mL in drinking water and treated water with No. of days of aerial exposure.

bottle for further studies. The weight of recovered Cu as $Cu(OH)_2$ was found to be 2.67 g (27.36 mmol) (Fig. 11; Scheme 4). In academic institutions, Cu is mainly used in its salt form. Hence we further converted $Cu(OH)_2$ to an aqueous solution of $CuSO_4$ by treating it with 2 M H_2SO_4. Following this $CuSO_4{\cdot}5H_2O$ crystal was obtained by slow evaporation of the solvent in a hot water bath. Net weight of $CuSO_4{\cdot}5H_2O$ was found to be 6.7 g (96 % of copper recovery).

3.6. Toxicity study of untreated water and comparison with treated water

To study the toxicity of untreated water, three conical flasks containing 100 mL of sterile water each were contaminated with freshly cultured *E. coli* (~ 10^5 CFU/mL). To flask I, 1 mL of drinking water was added, and to flasks II and III, 1 mL of untreated water and treated water were added respectively. All the flasks were kept in a rotary incubator shaker at 37℃ at 150 rpm. At the time interval of 2 h, the active bacterial population in the water sample was analyzed *via* serial dilution methods. The water sample in which untreated water was added (flask II) was found to be below the detectable limit after six hours. This is possible due to the toxic effect of the dyes on the bacteria. Whereas in the water sample of flasks I and III, the bacterial population was found to be almost the same (Fig. 12, Table S10). These results confirmed that the toxic wastewater after treatment became nontoxic.

Before discharging the treated water into the environment, it is important to confirm that the treated water is healthy enough for other microbes present in the environment as well. To test this, the survival of aerial microbes in the treated water was tested by adopting our previously reported methods with slight modification [35]. The beaker containing drinking water as a control and the beaker containing treated water as a test sample was kept in the open air for 3 days. With an increasing number of days of aerial exposure, the microbial contamination in both drinking and treated water samples was evaluated and found to be almost the same (Fig. 13, Table S11). Additionally, this simple method can be adopted to evaluate the quality of all other treated wastewater from academia and industries.

4. Conclusion

In this study, Cu_2O-laboratory waste was used as a Fenton-like catalyst for treating laboratory wastewater by implementing the concepts of the circular economy toward the development of economical, green, and sustainable laboratory waste management. The catalytic efficiency of Cu_2O towards the decomposition of crystal violet, methylene blue, and safranin was evaluated by making use of H_2O_2 as an oxidant. The catalyst was recycled and reused up to five catalytic cycles without significant loss of its catalytic activity. Additionally, laboratory wastewater containing all these toxic dyes was treated successfully using the same catalyst with excellent efficiency. Such copper-based waste can be used for the treatment of wastewater in an academic laboratory, which will help an institution to develop self-sustained waste management units. Post-water treatment, copper was recovered as copper sulphate pentahydrate with a 96 % of copper recovery. The limitation of this method lies in the fact that the catalyst is not recyclable when it's used against real laboratory wastewater. Indeed, the copper can be recovered by controlled alkaline treatment after completion of the reaction. Further, the survival of *E. coli* and other aerial microbes in the treated water was also evaluated and found to be healthy enough to be discharged into the environment.

CRediT authorship contribution statement

Randhir Rai: Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Amiliya Paulson:** Writing – review & editing, Methodology, Data curation.

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Declaration of Competing Interest

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

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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.scowo.2025.100073.

Data availability

Data will be made available on request.

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