Supporting Information

Deploying a copper catalyst for efficient degradation of commercial and industrial dyes in a two-stage wastewater treatment under practical conditions

Afsar Ali[a], Badri Vishal Meena[b], Naseer Ahmed Shah[c], Tannu[d], Chinmay Ghoroi[b], Arnab Dutta[c,d *]*

[a]Chemistry Discipline, Indian Institute of Technology Gandhinagar, Palaj, Gandhinagar, Gujarat 382355, India

[b]Chemical Engineering Discipline, Indian Institute of Technology Gandhinagar, Palaj, Gandhinagar, Gujarat 382355, India

[c]Chemistry Department, Indian Institute of Technology Bombay, Powai, Mumbai, Maharashtra 400076, India

[d]Interdisciplinary Program in Climate Studies, Indian Institute of Technology Bombay, Powai, Mumbai, Maharashtra 400076, India

Corresponding author: arnab.dutta@iitb.ac.in

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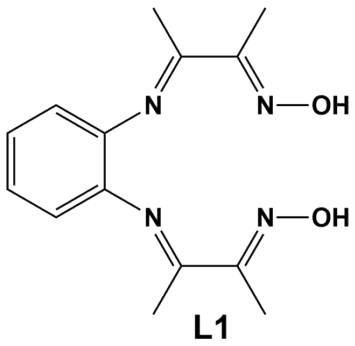
EXPERIMENTAL SECTION

Materials and Methods:

Acetone (HPLC and Spectroscopy), N,N-Dimethylformamide (HPLC and Spectroscopy), Diacetylmonoxime (AR), and Diethyl ether (AR) were purchased from SD Fine chemicals Ltd. India. Methanol (HPLC and gradient), Chloroform (AR/ACS), Hydrochloric acid (AR/ACS), Sodium Hydroxide (AR), and Sodium sulfate, anhydrous (AR/ACS) were purchased from Finar Chemicals Pvt. Ltd. 1,2 Phenylenediamine (AR), diacetyl monoxime (AR), $CuCl_2.2H_2O$ (AR), d_6-DMSO (NMR solvent), Rhodamine 6G (Rh-6G), Reactive Black-5 (RB-5), Direct blue 71(DB-71) were purchased Sigma-Aldrich India and all other commercial dyes except Rh-6G, RB-5, DB-71 were procured from TCI chemicals (India) Pvt. Ltd. Glassware was oven dried before use. Nuclear Magnetic Resonance Spectra (NMR) were recorded at 300K temperature using a Bruker Avance III 500 MHz Ascent FT spectrometer with working frequencies of 500 MHz for ^1H NMR. NMR signals are reported in ppm with solutions in $(CD_3)_2SO$ (δ= 2.50 ppm) solvent. UV-Vis spectra were recorded on a JASCO V-750 spectrophotometers using 1 cm path length in 1 mL Kozima make quartz cuvette. ATR-FTIR spectra of pure solid samples were recorded on PerkinElmer (Spectrum-Two) spectrometer. ESI Mass of the complexes was recorded with a synapt G2S ESI-QToF LCMS (Waters) in positive mode. Cyclic voltammetry (CV) experiments were carried out at room temperature using Metrohm Autolab PGSTAT 101 potentiostat. CO_2 gas peaks were recorded in CIC Dhruva Gas chromatography. A standard three electrode system under N_2 atmosphere was used with a 1 mm glassy carbon disc as a working electrode, Ag/AgCl (0.1 M $AgNO_3$) (in DMF) or Ag/AgCl (saturated KCl) (in aqueous solution) as a reference electrode connected by vycor tip and a platinum wire as a counter electrode. All potentials are reported versus $Fe(C_5H_5)_2^{+/0}$ (Ferrocene, $FeCp_2^{+/0}$) (in DMF) or $Fe(CN)_6^{3-/4-}$ couple ($E_{[Fe(CN)6]3-/4-}$ = +0.360 V vs. SHE) (in aqueous solution), added as an internal standard at the end of each measurement. Spectro-electrochemistry was performed at room temperature in DMF solution using Avantes Starline Avaspec-2048 spectrophotometer with 20.00 ms integration time and near 100 average scans. 2 mL of sample was placed in a 3.5 mL quartz cuvette (1 cm path length) placed in an external sample holder connected to the light source and detector via optical fibres. The system was further connected to Metrohm Autolab

PGSTAT 101 using a 3 mm glassy carbon rod as working electrode, Pt wire as a counter electrode, and Ag/AgCl (in saturated KCl) as a reference electrode with continuous N_2 pressure.

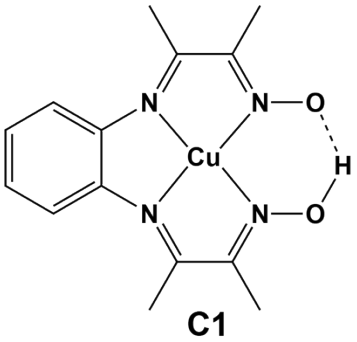
Preparation of 1,2 phenylenediimine-oxime ligand (L1):



L1

Methanolic solution (10 ml) of 2 eq. (202.22 mg, 2 mmol) diacetyl-monoxime was added with 1 eq. (108.14 mg, 1 mmol) of 1,2-phenylenediamine. A catalytic amount (10 µL) of hydrochloric acid was added to the reaction mixture and it was refluxed for 8 hours at 70 ˚C. The yellow coloured solid product was obtained as a final product, which was collected after removal of the solvent under reduced pressure. (Yield 80 %).^{1}H-NMR (500 MHz, DMSO-d_6) (δ/ppm): 11.30 (s, 2H), 8.00 (dd, 2H), 7.75 (dd, 2H), 1.97 (s, 6H), 2.70 (s, 6H). UV-vis (in DMF) (λ_{max} in nm, ε in parentheses $M^{-1}cm^{-1}$): 240 (35000), 310 (9500), 325 (shoulder, 8000). HRMS (G2S-ESI-QToF) m/z$^+$ calculated for (M+H$^+$) [$C_{14}H_{19}N_4O_2$]: calculated 275.14, experimentally observed 275.0368.

Preparation of 1,2 phenylenediimine-oxime copper complex (C1):



C1

One equivalent (170.48 mg, 1 mmol) blue coloured solution of $CuCl_2.2H_2O$ in methanol was added dropwise to a methanolic solution of one equivalent (274.31 mg, 1 mmol) of yellow coloured L1 ligand. The solution gradually turned into dark brown colour. This solution was stirred at room temperature for 1 hour followed by 2-hour reflux. The dark brown coloured solid product was obtained as a final product following the removal of the solvent under reduced pressure and drying the product under a high vacuum overnight. (Yield 65%) UV-vis (in DMF) (λ_{max} in nm, ε in parentheses $M^{-1}cm^{-1}$): 240 (25000), 275 (15000), 280 (shoulder, 11000), 320 (5000), 430 (shoulder, 4800), 460 (5000), 490 (shoulder, 4800), 850 (broad, 110). HRMS (G2S-ESI-QToF) m/z$^+$ calculated for (M+H$^+$) [$C_{14}H_{17}N_4O_2Cu_1$]: calculated 336.06, experimentally observed 336.3152.

Two-stage Catalytic setup for decolorization of commercial dyes and industrial effluents:

A two-stage catalytic setup was devised here for implementing an efficient dye-degradation strategy. In the first step, a set of physical (flocculation) and chemical adsorption (coagulation) was combined for an effective separation of organic dyes from industrial effluent sample solutions. Here, a mixture of $FeSO_4$ and CaO (1.0 g each) were utilized as adsorbates for cleansing of both dark-colored standard and industrial dyes (1.0-liter volume size) with approximately 30% adsorption efficiency. This initial physical treatment specifically precipitates out (dark brown colored) the insoluble and sparingly soluble dye molecule fragments present in the effluents. In stage two, the resultant clear brown solution was filtered (volume 1.0-liter) and treated with the synthetic copper complex **C1** (4.0 mg) in the presence of the stoichiometric amount of H_2O_2 (1.0 mL). This concoction of the **C1**/H_2O_2 mix triggers an advanced oxidation process (AOP) that primarily proceeds as a catalytic reaction. This H_2O_2-induced and copper complex-driven catalysis extensively degrades the water-soluble organic dye molecules to generate CO_2 as an exclusive side product, while the solution slowly turned light yellow to colorless over time. The continuous production of CO_2 during this AOP step was evident from the generation of the copious amount of gas bubbles and frothing of the solution. This hypothesis was further confirmed by the signature peak of CO_2 in gas chromatography.

This two-step setup, consisting of physical and chemical treatment modules, was utilized for screening of an array of twelve commercially available dyes along with four as-received industrial dyes (acquired from textile industries and dye industries) following the procedure mentioned in the above section. All dye degradation experiments were carried out using copper complex **C1** and H_2O_2 in stoichiometric amounts for an incubation period of 0.25-8.0 hours. The variation of the incubation period is primarily dependent on the concentration of the dye molecules in the sample.

The change in the optical spectra of the dye solution following the treatment of **C1** and H_2O_2 mix was followed via a JASCO-V750 UV-Visible spectrophotometer at room temperature. The as-prepared reaction mixtures containing dye molecules and **C1** / H_2O_2 mix were allowed to react at ambient temperature under air with a constant stirring (*500 rpm*). The percentage degradation efficiency was calculated by using initial and final absorbance with respect to the time and control experiments (in the presence of only H_2O_2 and $CuCl_2/H_2O_2$) process. After treatment, the complex **C1** was removed by means of filtration and centrifugation. The percentage degradation efficiency has been calculated by using the following formula:

$$\text{Percentage of dye degradation} = \left[\frac{Initial\ conc.\ -Final\ conc.}{Intial\ conc.}\right] \times 100$$

The initial concentration (before treatment) has been shown at zero time and final concentration (after treatment) at a certain time.

Methodology for GC (Gas Chromatography):

The amount of CO_2 evolved during the process (following dye oxidation) has been detected by using a Dhruva CIC gas chromatography (GC) instrument equipped with TCD detector having a 5Å molecular sieve column while deploying Ar as carrier gas. In the beginning, we prepared 1.0 mM dyes solution in distilled water. During the experimental setup, we took 4.0 ml of dye solutions in a 20.0 ml airtight vial along with a small magnetic bead. Copper complex and H_2O_2 were added as catalyst and oxidizing partner, respectively. After that, we stirred the mixture solution at 500 rpm for all the samples under the nitrogen saturated condition. The headspace gas has been collected after one hour intervals with an Agilent manual syringe (capacity 1.0 ml) till 8 hours of complete degradation study. The control experiments were also performed under analogous conditions to measure the background CO_2. During the gas detection, only CO_2 was detected as major product along with a small amount of CO. The absence of any significant mass spectral signal of the precursor dyes following the degradation study revealed the complete degradation of dyes during experiments.

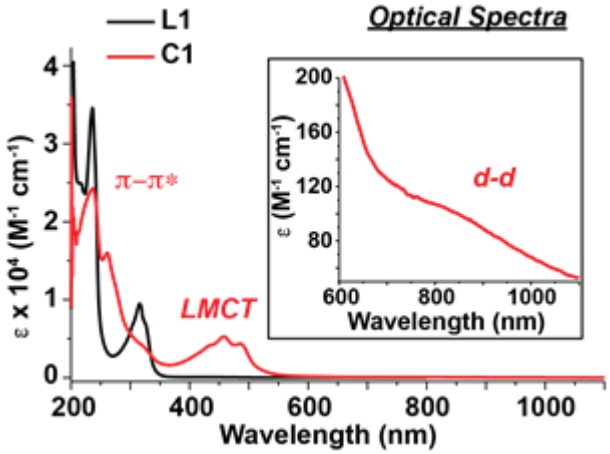


Figure S1. Comparative optical spectra recorded for ligand L1 (black trace) and complex C1 (red trace) in DMF exhibiting π–π* and LMCT transitions at room temperature. The inset exhibits d–d transition recorded for C1 under the same condition. Reprinted with permission from[1]. Copyright 2021 American Chemical Society.

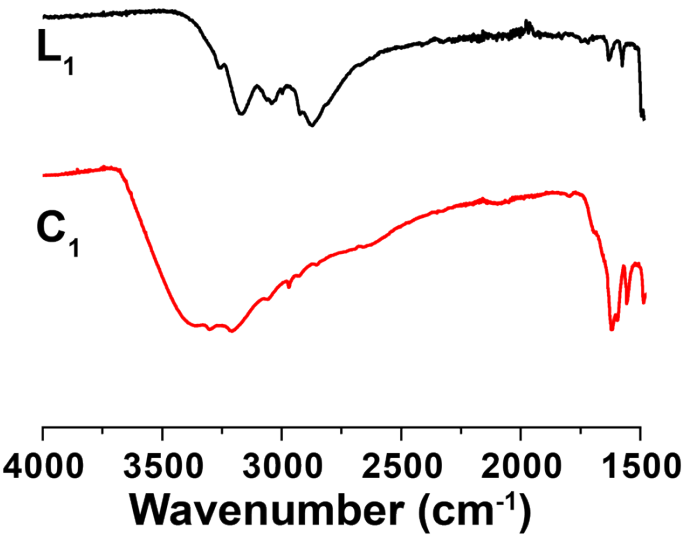


Figure S2. Comparative FTIR spectra in the 4000-1500 cm^{-1} region for L1 (black trace) and C1 (red trace) measured with powder sample. The 3700-3000 cm^{-1} region exhibited a broad feature in C1 compared to sharp features observed in L1. Reprinted with permission from[1]. Copyright 2021 American Chemical Society.

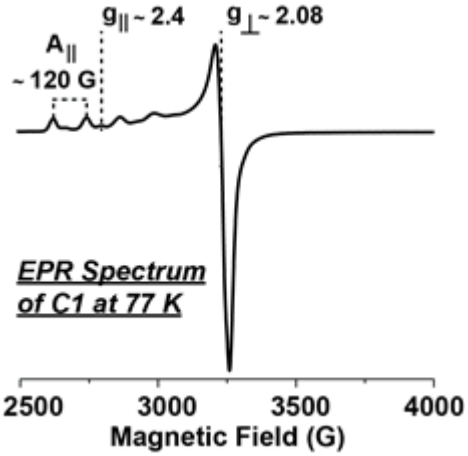


Figure S3. The axial EPR spectrum recorded for C1 in DMF at 77 K (black trace) displaying the $g_{\|}$, $g_{\perp}$, and $A_{\|}$ values. Reprinted with permission from[1]. Copyright 2021 American Chemical Society.

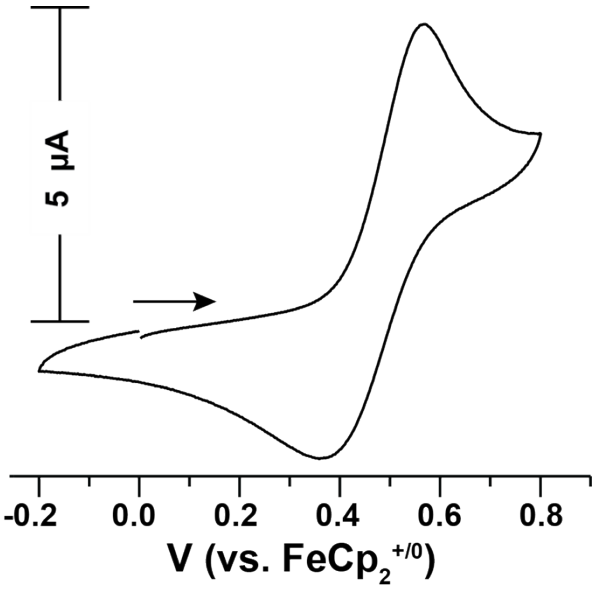


Figure S4. Cyclic Voltammogram (CV) of 0.5 mM C1 recorded in DMF with 1 mm diameter glassy carbon disc working electrode, Pt wire counter electrode, and Ag/AgCl (in 0.1 M $AgNO_3$) reference electrode. This CV is recorded in the presence of 0.1 M nBu_4NBF_4 electrolyte under 1 atm N_2 atmosphere with 0.2 V/s scan rate. The horizontal arrow denotes the initial scan direction. Reprinted with permission from[1]. Copyright 2021 American Chemical Society.

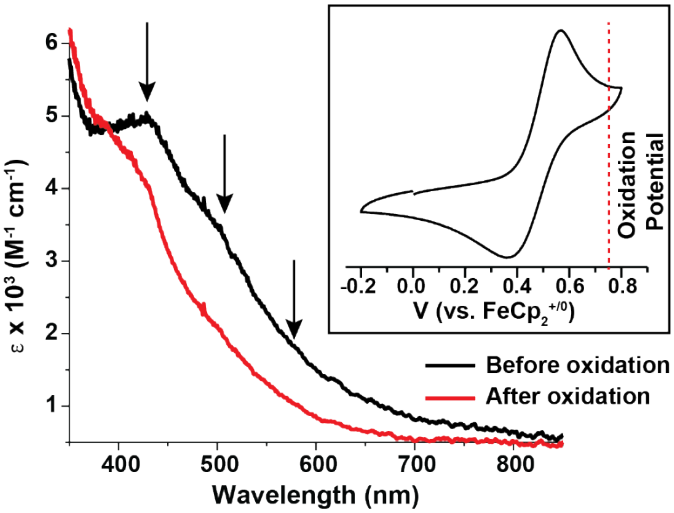


Figure S5. The changes observed in the LMCT bands of C1 in DMF solution during spectroelectrochemistry experiment before (black trace) and after (red trace) the oxidation process. A chronocoulometric experiment was performed with a sample where the potential of the system was held at 0.75 V (vs. $FeCp_2^{+/0}$) as indicated by the horizontal red dashed line in the inset. The horizontal black arrows display the change in the LMCT bands. This data was recorded with 1 mm diameter glassy carbon rod working electrode, Pt wire counter electrode, and Ag/AgCl (in 0.1 M $AgNO_3$) reference electrode in the presence of 0.1 M nBu_4NBF_4 electrolyte under N_2 atmosphere. Reprinted with permission from[1]. Copyright 2021 American Chemical Society.

Optical and percentage degradation study for standard dye and dye effluents:

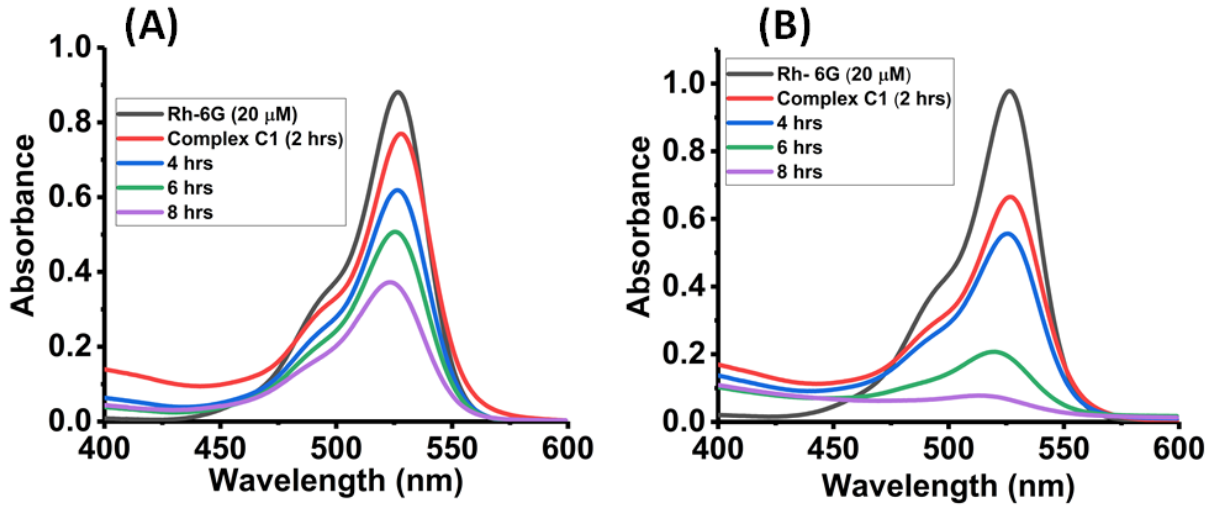


Figure S6. (A) The Optical spectral study recorded for degradation of Rh-6G (20 μM) in pH 3.0 aqueous condition (B) in pH 7.0 aqueous condition, treated with complex C1 (5 μM) and H_2O_2 (12.5 μM) for 8 hrs incubation. The optical spectra with black trace exhibited for Rh-6G before treatment, the degradation, after 2 hrs (red trace), 4 hrs (blue trace), 6 hrs (green trace) and 8 hrs (violet trace) have been recorded with complex C1/H_2O_2 and same trace in case of pH 7.0.

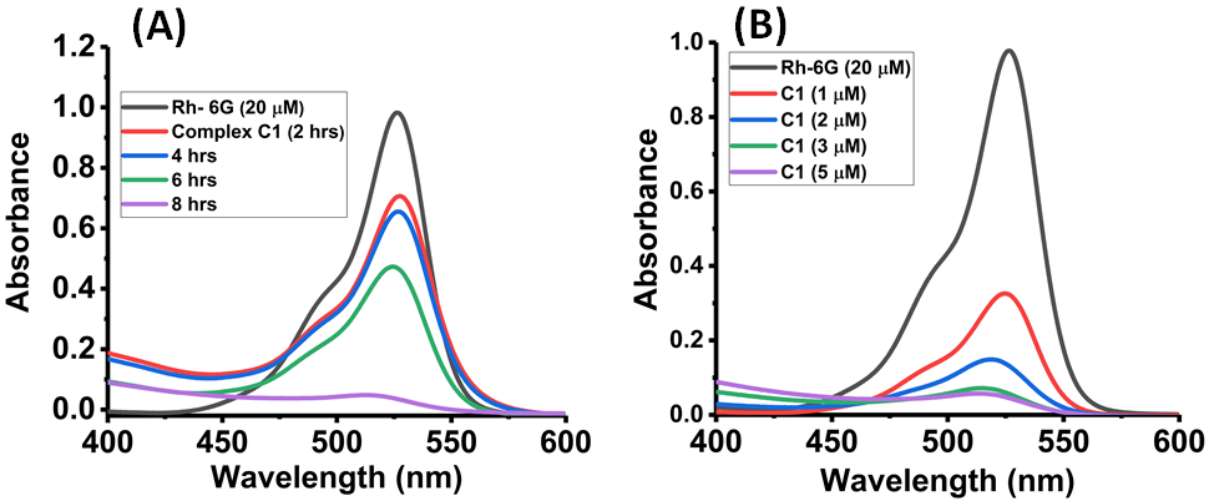


Figure S7. (A) The Optical spectral study recorded for degradation of Rh-6G (20 μM) in pH 11.0 aqueous condition, treated with complex C1 (5 μM) and H_2O_2 (12.5 μM) for 8 hrs incubation. The optical spectra with black trace exhibited for Rh-6G before treatment and the degradation after 2 hrs (red trace), 4 hrs (blue trace), 6 hrs (green trace) and 8 hrs (violet trace) have been recorded with complex C1/H_2O_2. (B) The Optical spectral study recorded for degradation of Rh-6G (20 μM) in pH 7.0 aqueous condition at different concentrations of complex C1/H_2O_2 for 8 hrs incubation. The optical spectra with black trace exhibited for Rh-6G before treatment and the degradation after treatment with 1 μM complex C1/H_2O_2 (H_2O_2, 2.5 μM) (red trace), 2 μM complex C1/H_2O_2 (H_2O_2, 5 μM) (blue trace), 3 μM complex C1/H_2O_2 (H_2O_2, 7.5 μM) (green trace) and 5 μM complex C1/H_2O_2 (H_2O_2, 12.5 μM) (violet trace) after 8 hrs incubation.

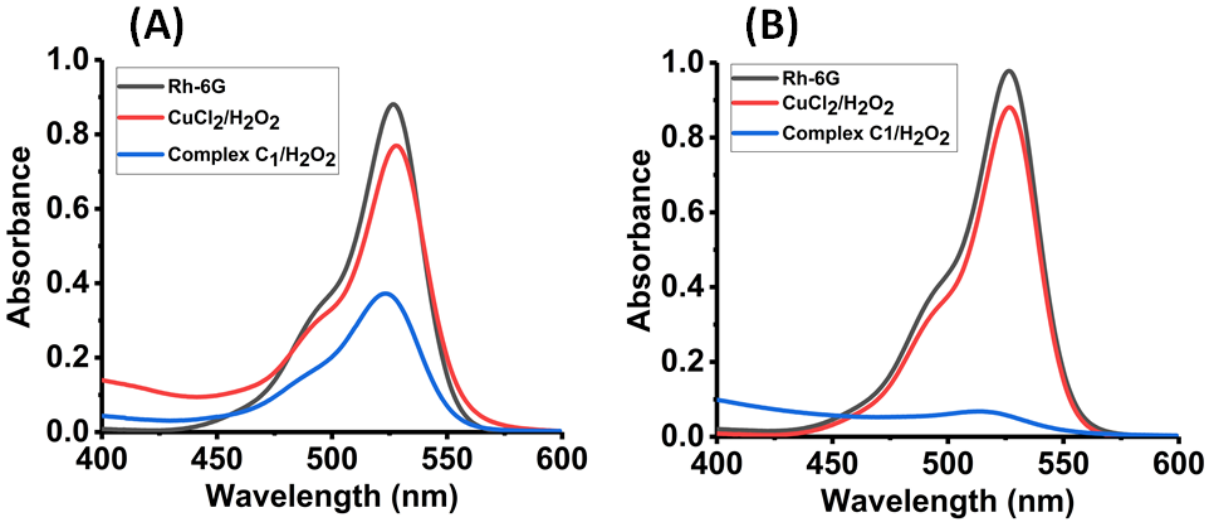


Figure S8. (B) The Optical spectral study recorded for degradation of Rh-6G (20 μM) in pH 3.0 aqueous condition (B) in pH 7.0 aqueous condition, treated with $CuCl_2$ (5 μM)/H_2O_2 (12.5 μM) and complex C1 (5 μM)/H_2O_2 (12.5 μM) for 8 hrs incubation. The optical spectra with black trace exhibited for Rh-6G before treatment and the degradation after treatment with $CuCl_2$/H_2O_2 (red trace) and treatment with complex C1/H_2O_2 (blue trace) after 8 hrs incubation.

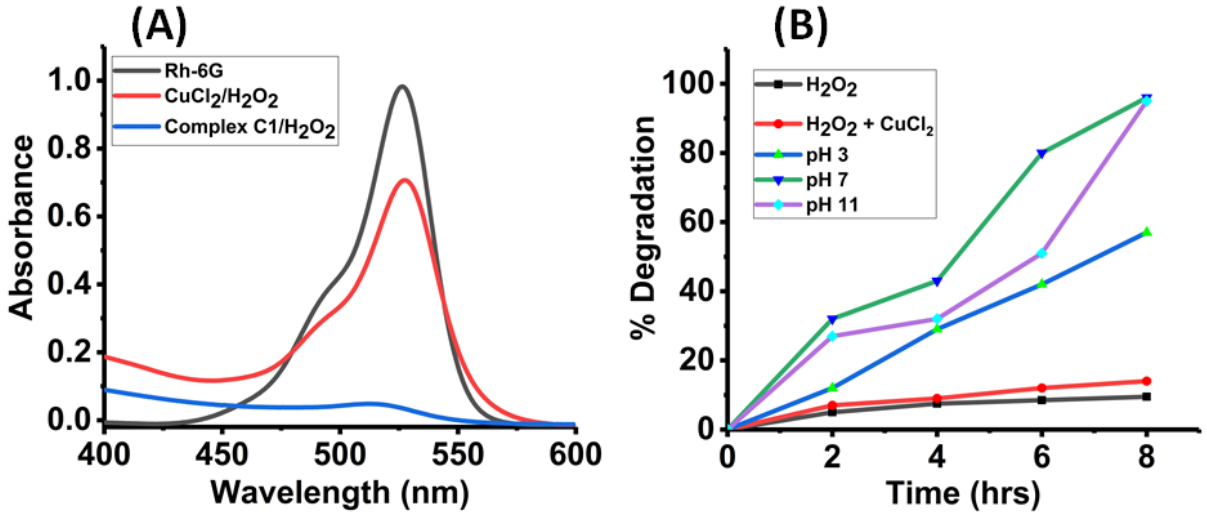


Figure S9. (A) The Optical spectral study recorded for degradation of Rh-6G (20 μM) in pH 11.0 aqueous condition, which has treated with $CuCl_2$ (5 μM)/H_2O_2 (12.5 μM) and complex C1 (5 μM)/H_2O_2 for 8 hrs incubation. The optical spectra with black trace exhibited for Rh-6G before treatment and the degradation after treated with $CuCl_2$/H_2O_2 (red trace) and treated with complex C1/H_2O_2 (blue trace) after 8 hrs incubation (B) The percentage degradation recorded for Rh-6G (20 μM) in different pH aqueous condition, which has treated with complex C1 (5 μM)/H_2O_2 (12.5 μM) for 8 hrs incubation. The optical spectra with black trace exhibited for Rh-6G treated with H_2O_2 only, red trace treated with $CuCl_2$/H_2O_2, blue trace treated with complex C1/H_2O_2 at pH-3, green trace treated with complex C1/H_2O_2 at pH-7 and violet trace treated with complex C1/H_2O_2 at pH-11.

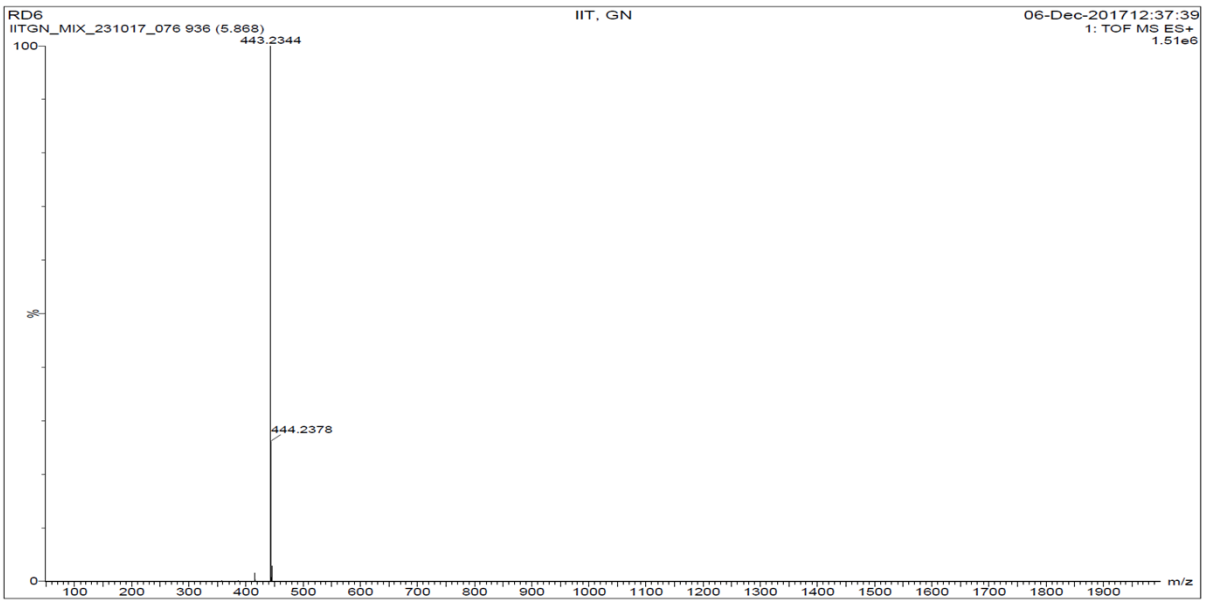


Figure S10. Mass spectra recorded for standard Rh-6G before treatment, which shown m/z = 443.23.

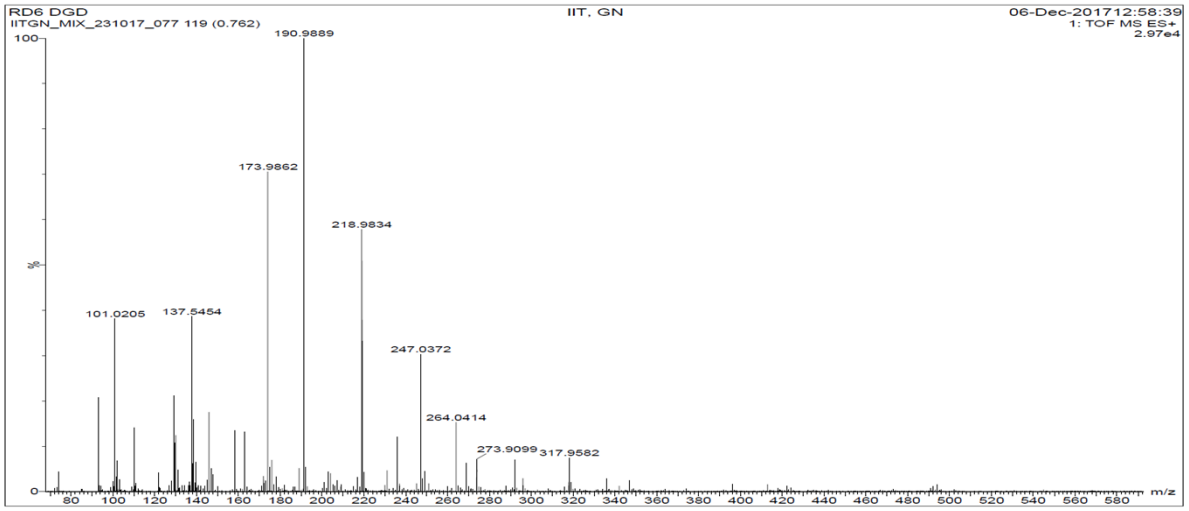


Figure S11. Mass spectra recorded for standard Rh-6G after 30 minutes of treatment with complex C1/H_2O_2. However, mass spectral peak related to Rh-6G was not observed, which indicated that Rh-6G is defragmented following the chemical treatment.

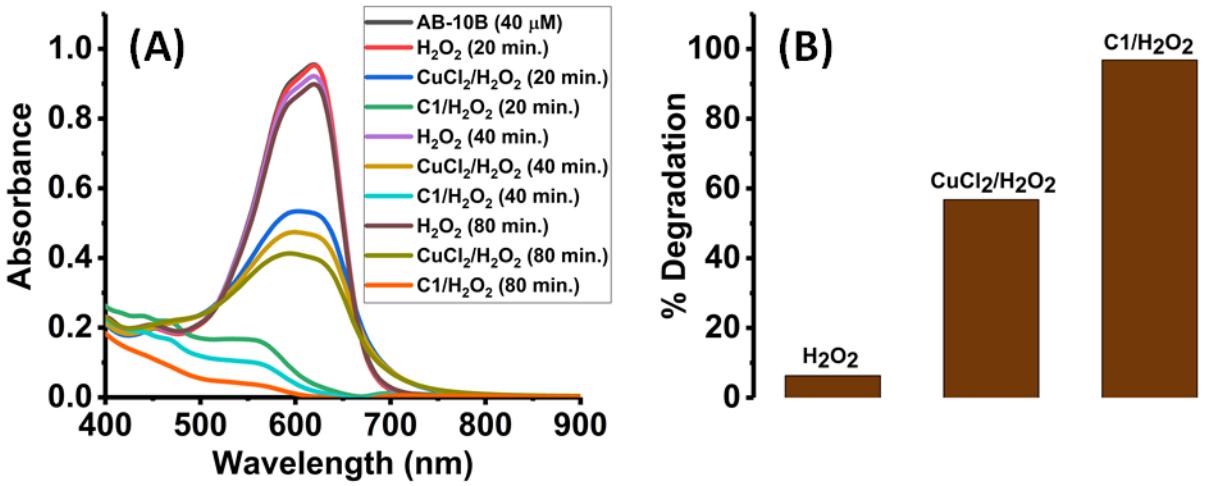


Figure S12. (A) Optical spectra recorded for AB-10B (Amido Black 10B) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 80 minutes. Black trace for AB-10B before treatment, red trace after 20 min. in presence of H_2O_2, blue trace after 20 min. in presence of $CuCl_2/H_2O_2$, green trace after 20 min. in presence of $C1/H_2O_2$. violet trace after 40 min. in presence of H_2O_2, light orange trace after 40 min. in presence of $CuCl_2/H_2O_2$, sky blue trace after 40 min. in presence of $C1/H_2O_2$, purple trace after 80 min. in presence of H_2O_2, light green trace after 80 min. in presence of $CuCl_2/H_2O_2$, and orange trace after 80 min. in presence of $C1/H_2O_2$ (B) The percentage degradation of AB-10B in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 80 min., which shown better degradation efficiency in $C1/H_2O_2$.

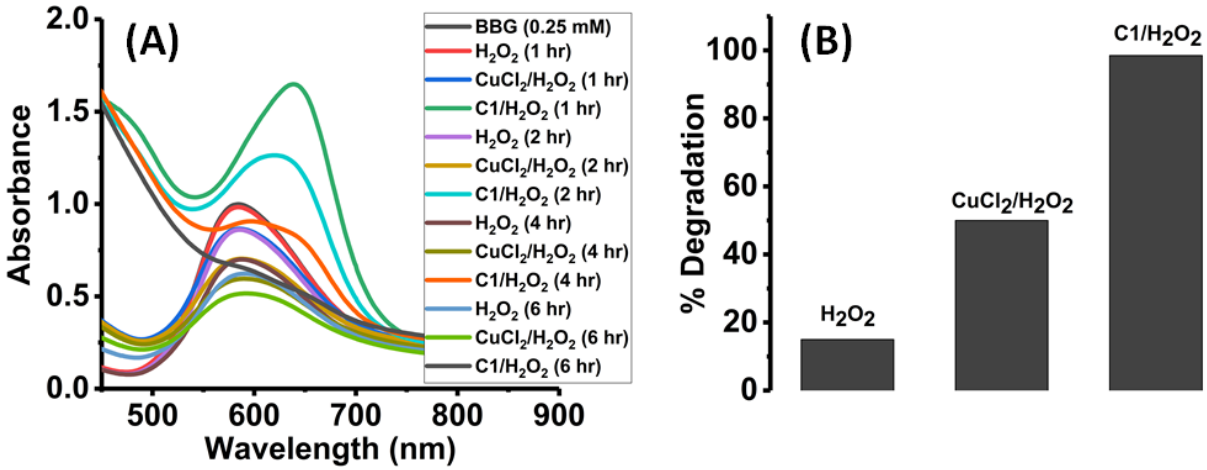


Figure S13. (A) Optical spectra recorded for BBG (Brilliant blue G) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 6 hrs. incubation. Black trace for BBG before treatment, red trace after 1 hr in presence of H_2O_2, blue trace after 1 hr in presence of $CuCl_2/H_2O_2$, green trace after 1 hr. in presence of $C1/H_2O_2$, violet trace after 2 hrs in presence of H_2O_2, light orange trace after 2 hrs in presence of $CuCl_2/H_2O_2$, sky blue trace after 2 hrs in presence of $C1/H_2O_2$, purple trace after 4 hrs in presence of H_2O_2, light green trace after 4 hrs in presence of $CuCl_2/H_2O_2$, orange trace after 4 hrs in presence of $C1/H_2O_2$, light blue after 8 hrs in presence of H_2O_2, light green trace after 8 hrs in presence of $CuCl_2/H_2O_2$, grey trace after 8 hrs in presence of $C1//H_2O_2$ (B) The percentage degradation of BBG in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 6 hrs. incubation.

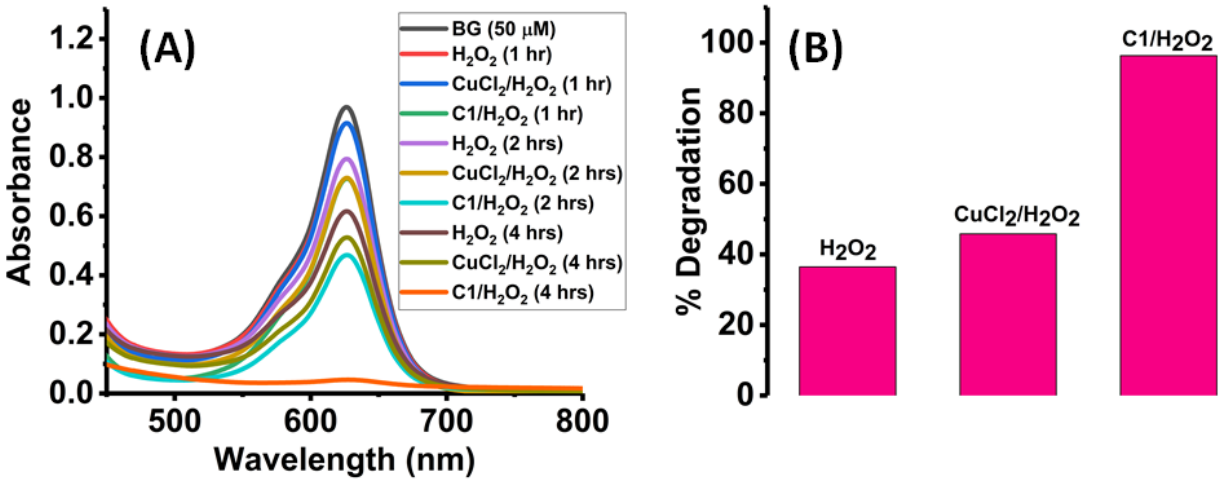


Figure S14. (A) Optical spectra recorded for BG (Brilliant green) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 4 hrs. Black trace for BG before treatment, red trace after 1 hr in presence of H_2O_2, blue trace after 1 hr in presence of $CuCl_2/H_2O_2$, green trace after 1 hr. in presence of $C1/H_2O_2$, violet trace after 2 hrs in presence of H_2O_2, light orange trace after 2 hrs in presence of $CuCl_2/H_2O_2$, sky blue trace after 2 hrs in presence of $C1/H_2O_2$, purple trace after 4 hrs in presence of H_2O_2, light green trace after 4 hrs in presence of $CuCl_2/H_2O_2$, orange trace after 4 hrs in presence of $C1/H_2O_2$. (B) The percentage degradation of BG in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 4 hrs.

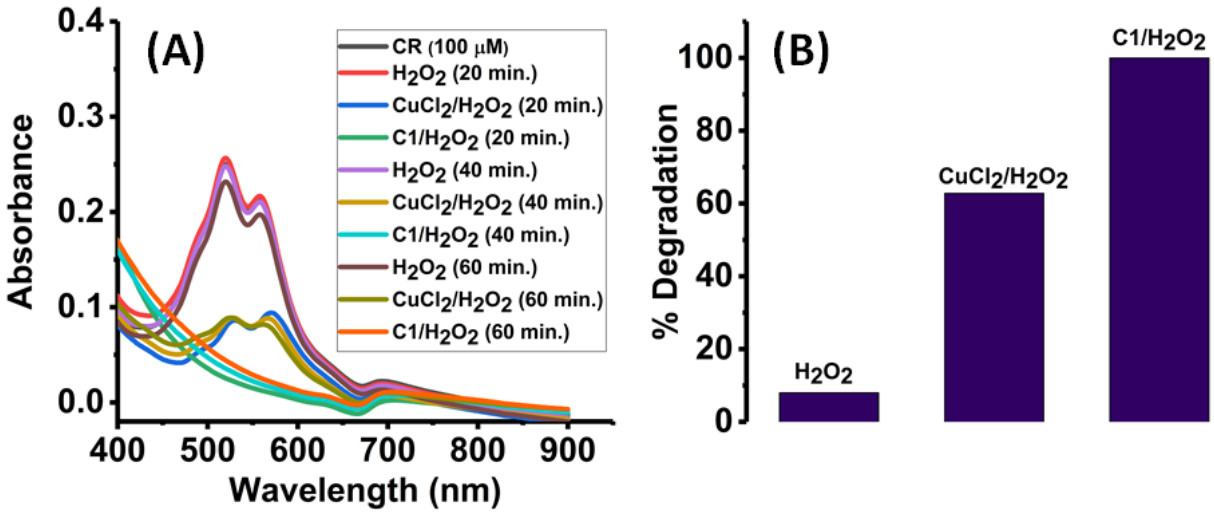


Figure S15. (A) Optical spectra recorded for CR (Carmine) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 60 min. Black trace for CR before treatment, red trace after 20 min. in presence of H_2O_2, blue trace after 20 min. in presence of $CuCl_2/H_2O_2$, green trace after 20 min. in presence of $C1/H_2O_2$, violet trace after 40 min. in presence of H_2O_2, light orange trace after 40 min. in presence of $CuCl_2/H_2O_2$, sky blue trace after 40 min. in presence of $C1/H_2O_2$, purple trace after 60 min. in presence of H_2O_2, light green trace after 60 min. in presence of $CuCl_2/H_2O_2$, orange trace after 60 min. in presence of $C1/H_2O_2$. (B) The percentage degradation of CR in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 1 hr.

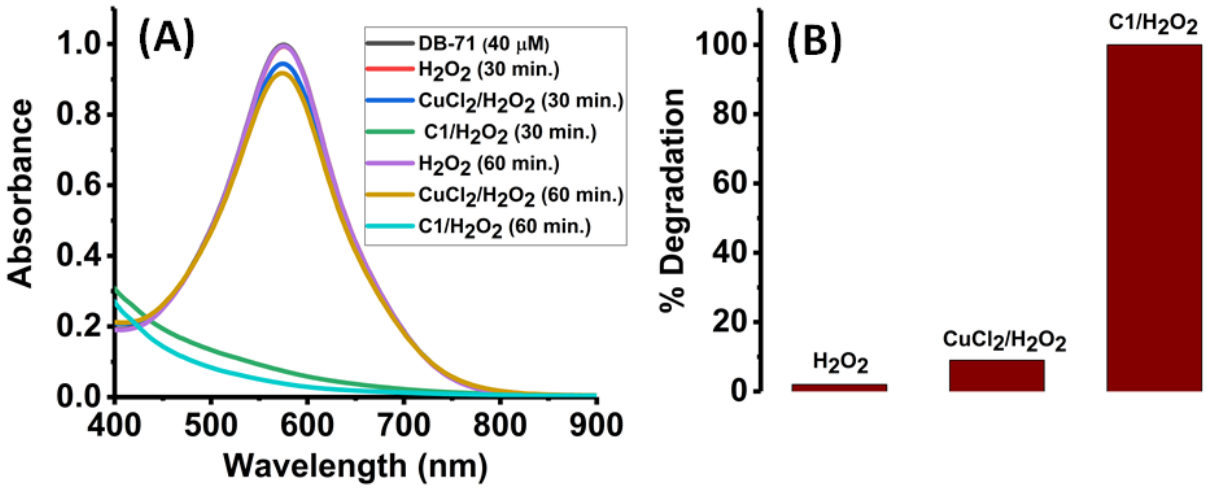


Figure S16. (A) Optical spectra recorded for DB-71 (Direct blue-71) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 60 min. Black trace for DB-71 before treatment, red trace after 30 min. in presence of H_2O_2, blue trace after 30 min. in presence of $CuCl_2/H_2O_2$, green trace after 30 min. in presence of $C1/H_2O_2$, violet trace after 60 min. in presence of H_2O_2, light orange trace after 60 min. in presence of $CuCl_2/H_2O_2$, sky blue trace after 60 min. in presence of $C1/H_2O_2$. (B) The percentage degradation of DB-71 in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 1 hr.

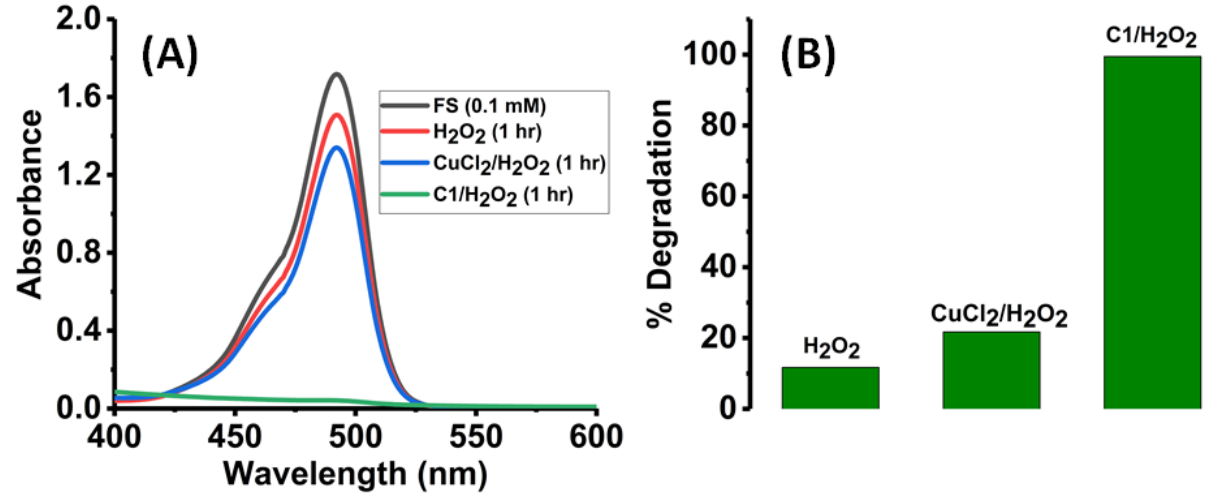


Figure S17. (A) Optical spectra recorded for FS (Fluorescein) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 60 min. Black trace for FS before treatment, red trace after 1 hr in presence of H_2O_2, blue trace after 1 hr min. in presence of $CuCl_2/H_2O_2$, green trace after 1 hr in presence of $C1/H_2O_2$. (B) The percentage degradation of FS in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 1 hr.

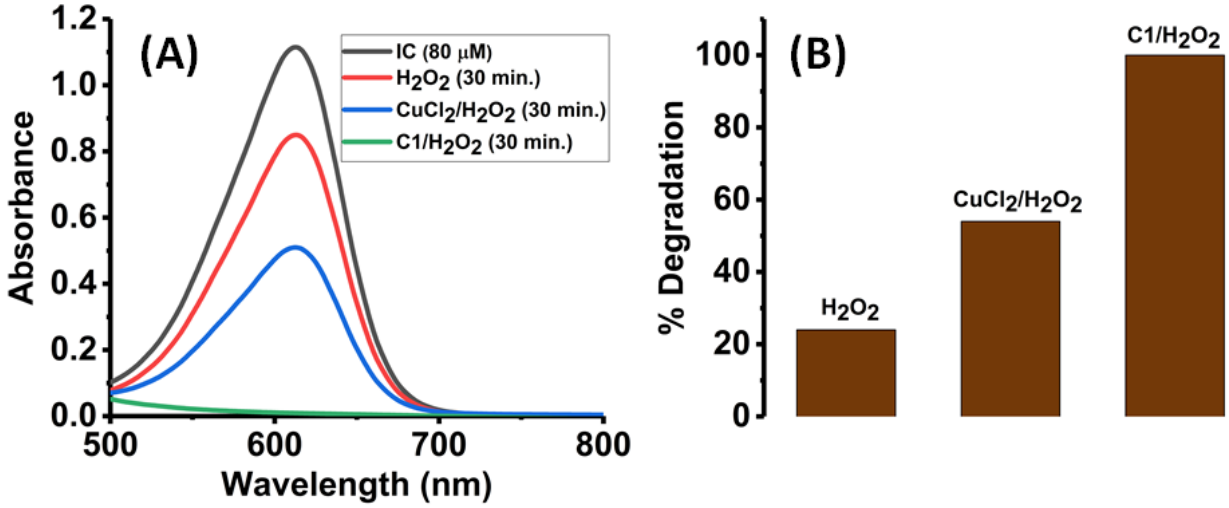


Figure S18. (A) Optical spectra recorded for IC (Indigo Carmine) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 30 min. Black trace for IC before treatment, red trace after 30 min. in presence of H_2O_2, blue trace after 30 min. in presence of $CuCl_2/H_2O_2$, green trace after 30 min. in presence of $C1/H_2O_2$. (B) The percentage degradation of IC in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 30 min.

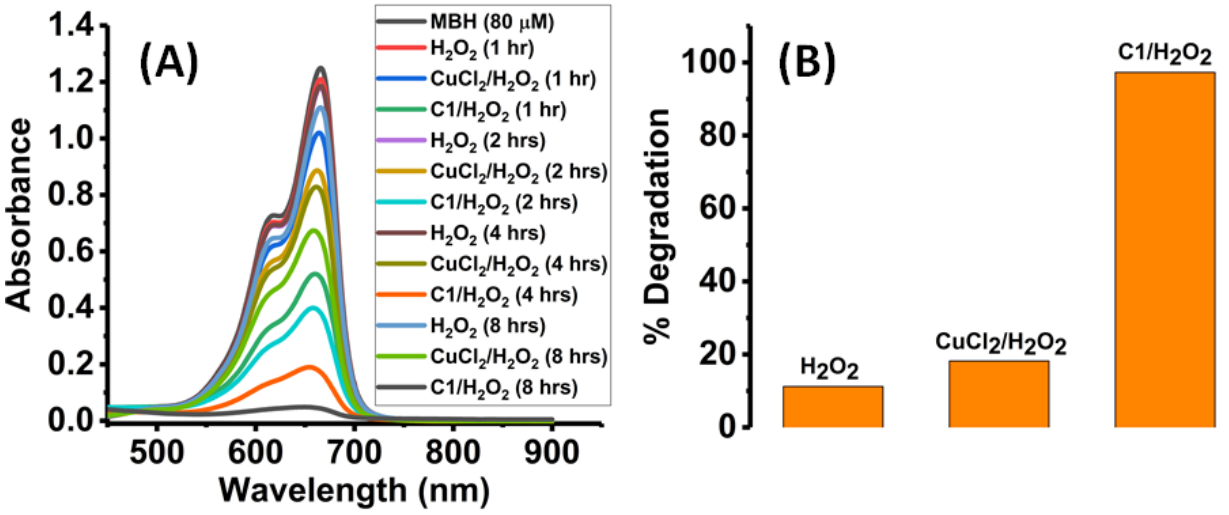


Figure S19. (A) Optical spectra recorded for MBH in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 8 hrs. Black trace for MBH before treatment, red trace after 1 hr in presence of H_2O_2, blue trace after 1 hr in presence of $CuCl_2/H_2O_2$, green trace after 1 hr. in presence of $C1/H_2O_2$, violet trace after 2 hrs in presence of H_2O_2, light orange trace after 2 hrs in presence of $CuCl_2/H_2O_2$, sky blue trace after 2 hrs in presence of $C1/H_2O_2$, purple trace after 4 hrs in presence of H_2O_2, light green trace after 4 hrs in presence of $CuCl_2/H_2O_2$, orange trace after 4 hrs in presence of $C1/H_2O_2$, light blue after 8 hrs in presence of H_2O_2, light green trace after 8 hrs in presence of $CuCl_2/H_2O_2$, grey trace after 8 hrs in presence of $C1//H_2O_2$ (B) The percentage degradation of MBH in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 8 hrs.

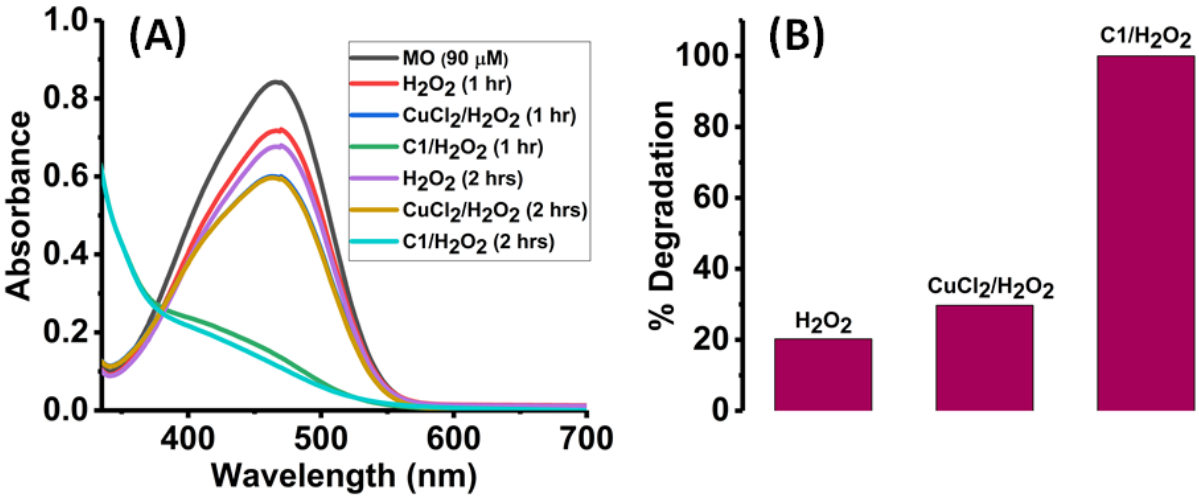


Figure S20. (A) Optical spectra recorded for MO (Methyl Orange) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 2 hrs. Black trace for MO before treatment, red trace after 1 hr in presence of H_2O_2, blue trace after 1 hr in presence of $CuCl_2/H_2O_2$, green trace after 1 hr. in presence of $C1/H_2O_2$, violet trace after 2 hrs in presence of H_2O_2, light orange trace after 2 hrs in presence of $CuCl_2/H_2O_2$, sky blue trace after 2 hrs in presence of $C1/H_2O_2$ (B) The percentage degradation of MO in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 2 hrs.

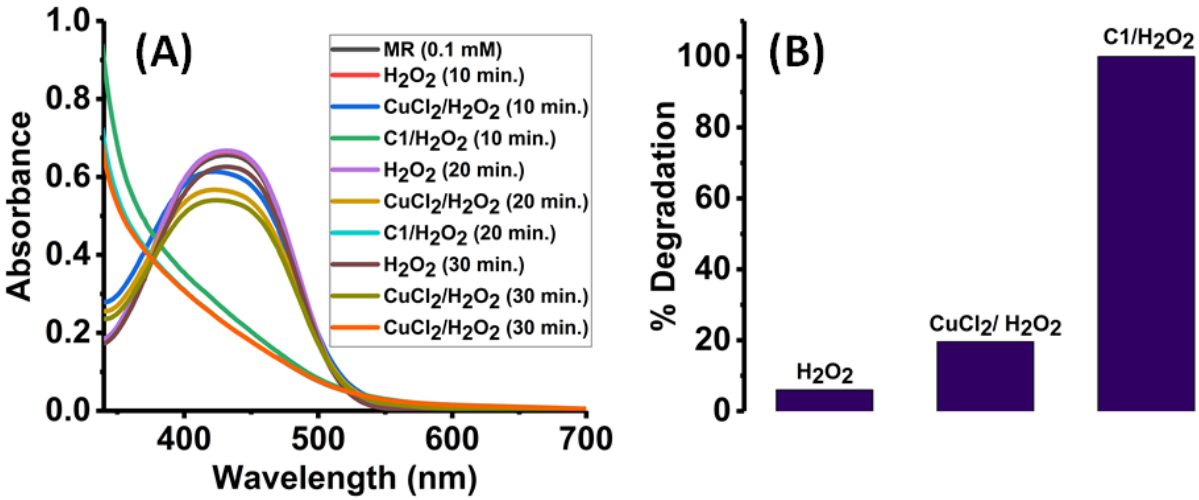


Figure S21. (A) Optical spectra recorded for MR (Methyl Red) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 30 min. Black trace for MR before treatment, red trace after 10 min. in presence of H_2O_2, blue trace after 10 min. in presence of $CuCl_2/H_2O_2$, green trace after 10 min in presence of $C1/H_2O_2$, violet trace after 20 min. in presence of H_2O_2, light orange trace after 20 min. in presence of $CuCl_2/H_2O_2$, sky blue trace after 20 min. in presence of $C1/H_2O_2$, purple trace after 30 min. in presence of H_2O_2, light green trace after 30 min. in presence of $CuCl_2/H_2O_2$, orange trace after 30 min. in presence of $C1/H_2O_2$ (B) The percentage degradation of MR in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 30 min.

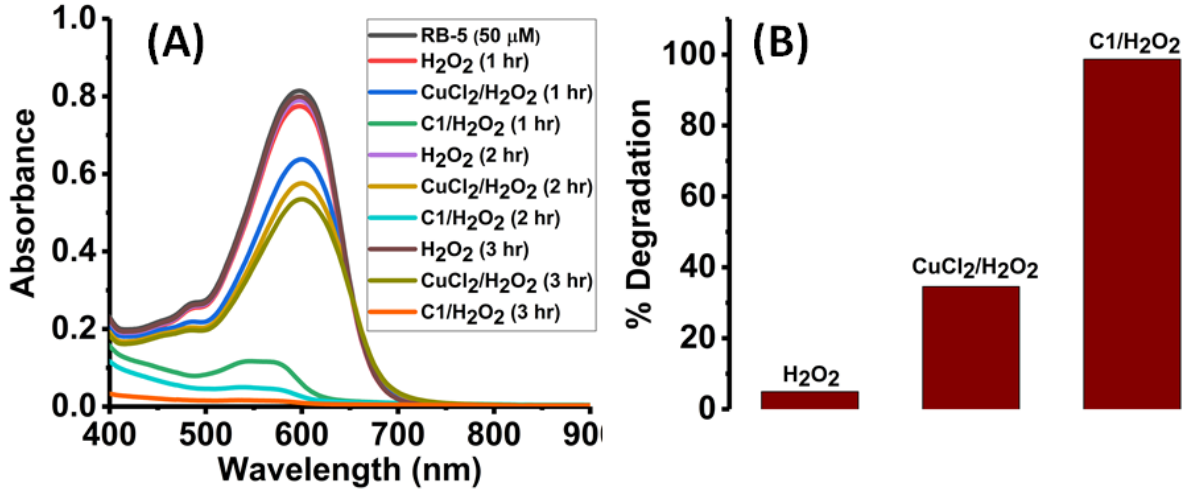


Figure S22. (A) Optical spectra recorded for RB-5 (Reactive Black-5) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 3 hrs. Black trace for RB-5 before treatment, red trace after 1 hr in presence of H_2O_2, blue trace after 1 hr in presence of $CuCl_2/H_2O_2$, green trace after 1 hr. in presence of $C1/H_2O_2$, violet trace after 2 hrs in presence of H_2O_2, light orange trace after 2 hrs in presence of $CuCl_2/H_2O_2$, sky blue trace after 2 hrs in presence of $C1/H_2O_2$, purple trace after 3 hrs in presence of H_2O_2, light green trace after 3 hrs in presence of $CuCl_2/H_2O_2$, orange trace after 3 hrs in presence of $C1/H_2O_2$. (B) The percentage degradation of RB-5 in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 3 hrs.

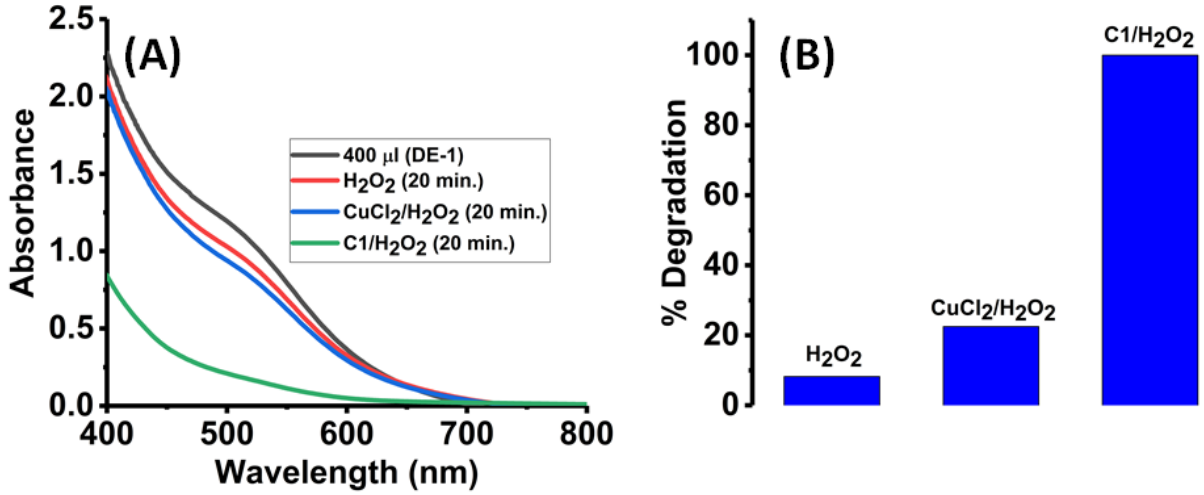


Figure S23. (A) Optical spectra recorded for DE-1 (Dye Effluent-1) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 20 min. Black trace for DE-1 before treatment, red trace after 20 min in presence of H_2O_2, blue trace after 20 min in presence of $CuCl_2/H_2O_2$, green trace after 20 min in presence of $C1/H_2O_2$. (B) The percentage degradation of DE-1 in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 20 min.

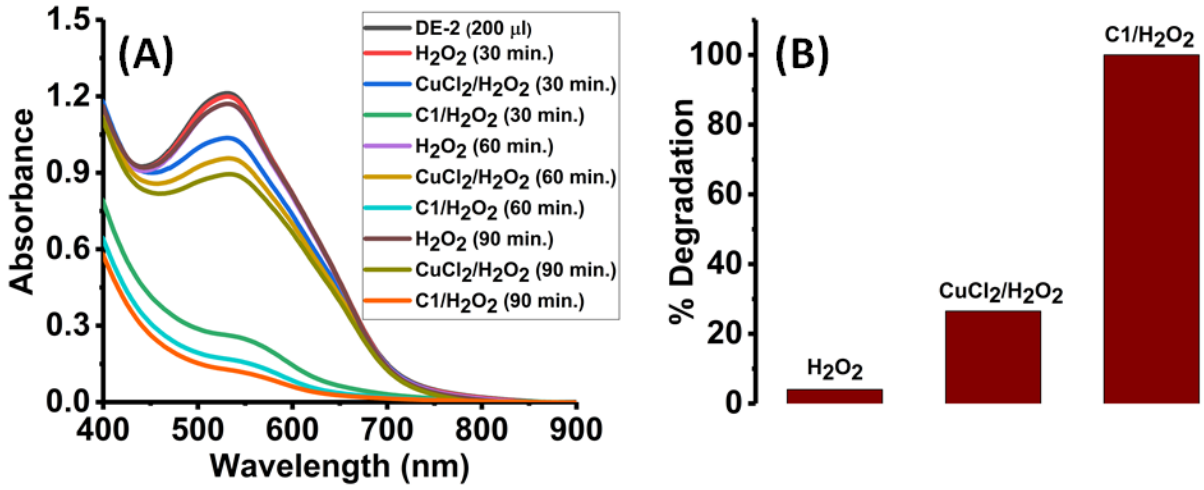


Figure S24. (A) Optical spectra recorded for DE-2 (Dye Effluent-2) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 90 min. Black trace for DE-2 before treatment, red trace after 30 min in presence of H_2O_2, blue trace after 30 min in presence of $CuCl_2/H_2O_2$, green trace after 30 min in presence of $C1/H_2O_2$, violet trace after 60 min in presence of H_2O_2, light orange trace after 60 min in presence of $CuCl_2/H_2O_2$, sky blue trace after 60 min in presence of $C1/H_2O_2$, purple trace after 90 min in presence of H_2O_2, light green trace after 90 min in presence of $CuCl_2/H_2O_2$, orange trace after 90 min in presence of $C1/H_2O_2$. (B) The percentage degradation of DE-2 in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 90 min.

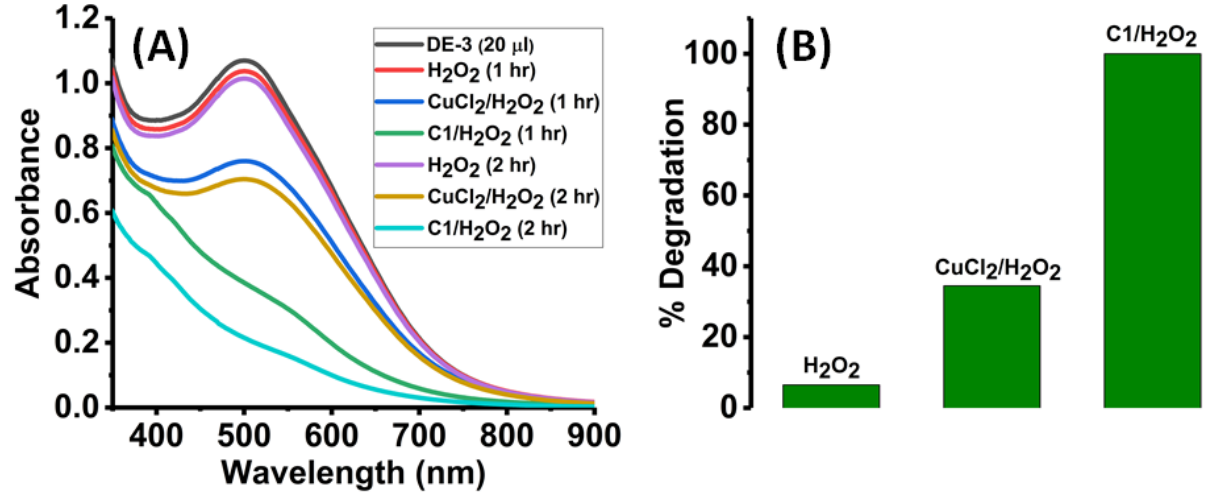


Figure S25. (A) Optical spectra recorded for DE-3 (Dye Effluent-3) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 2 hrs. Black trace for DE-3 before treatment, red trace after 1 hr in presence of H_2O_2, blue trace after 1 hr in presence of $CuCl_2/H_2O_2$, green trace after 1 hr in presence of $C1/H_2O_2$, violet trace after 2 hrs in presence of H_2O_2, light orange trace after 2 hrs in presence of $CuCl_2/H_2O_2$, sky blue trace after 2 hrs in presence of $C1/H_2O_2$. (B) The percentage degradation of DE-3 in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 2 hrs.

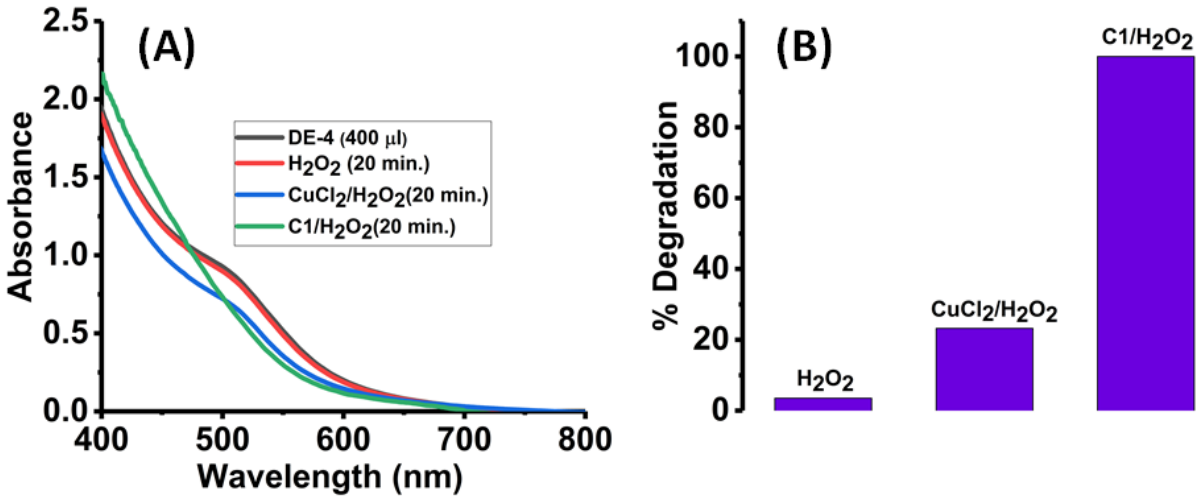


Figure S26. (A) Optical spectra recorded for DE-4 (Dye Effluent-4) in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ for 20 min. Black trace for DE-4 before treatment, red trace after 20 min in presence of H_2O_2, blue trace after 20 min in presence of $CuCl_2/H_2O_2$, green trace after 20 min in presence of $C1/H_2O_2$ (B) The percentage degradation of DE-4 in presence of H_2O_2, $CuCl_2/H_2O_2$ and $C1/H_2O_2$ after 20 min.

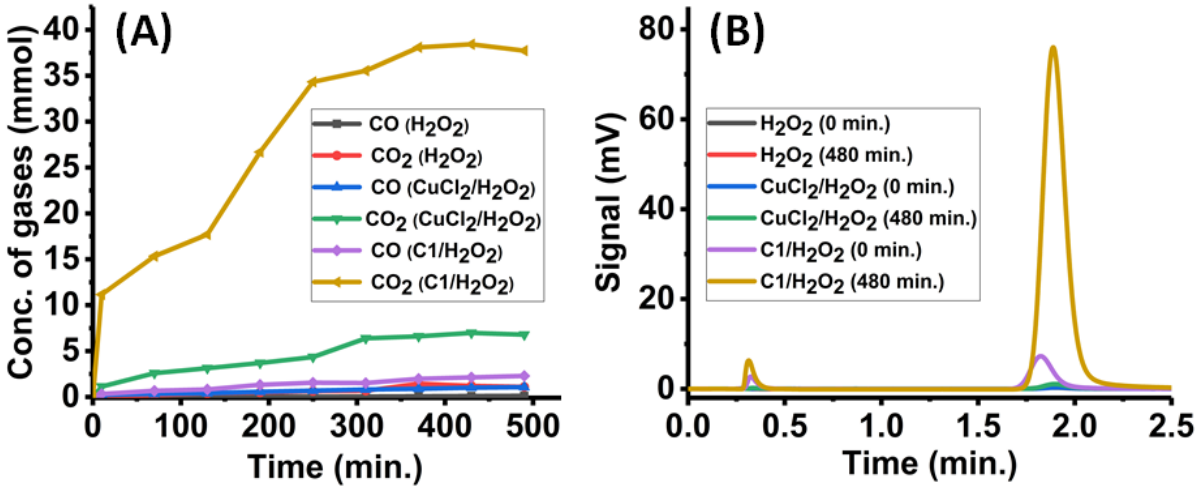


Figure S27. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of Rh-6G, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of Rh-6G. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

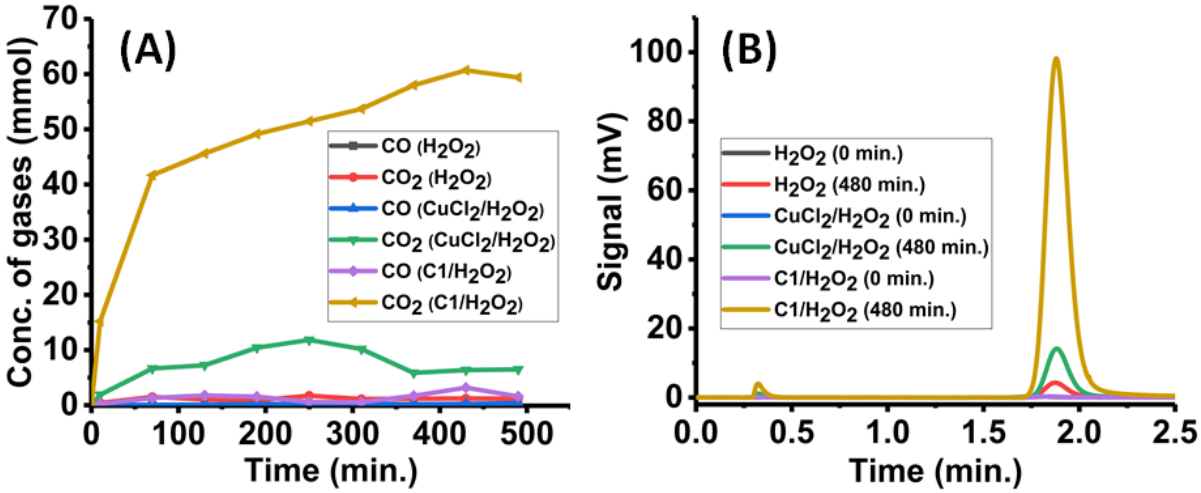


Figure S28. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of AB-10B, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of AB-10B. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

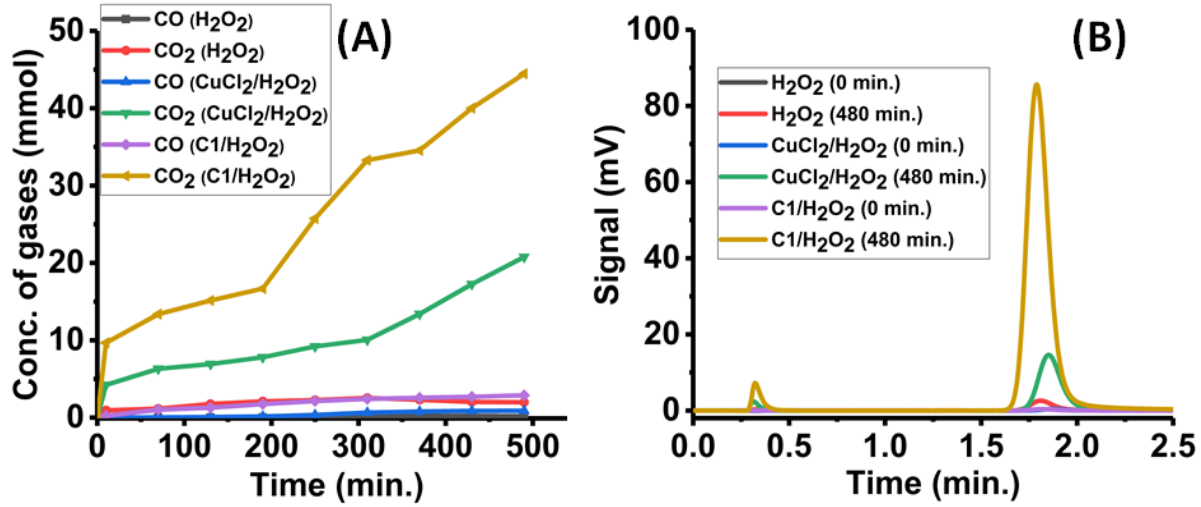


Figure S29. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of BBG, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of BBG. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

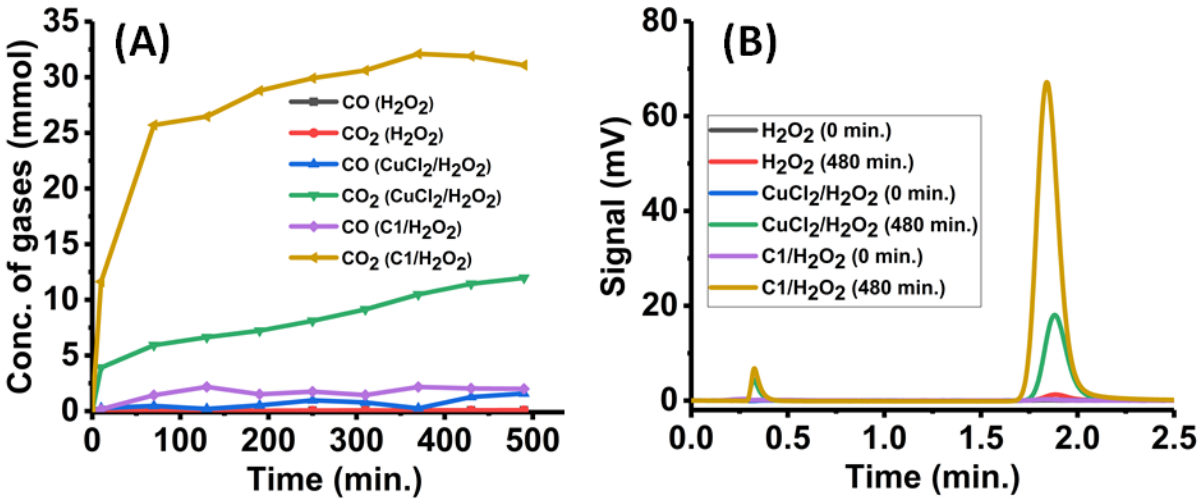


Figure S30. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of BG, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of BG. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

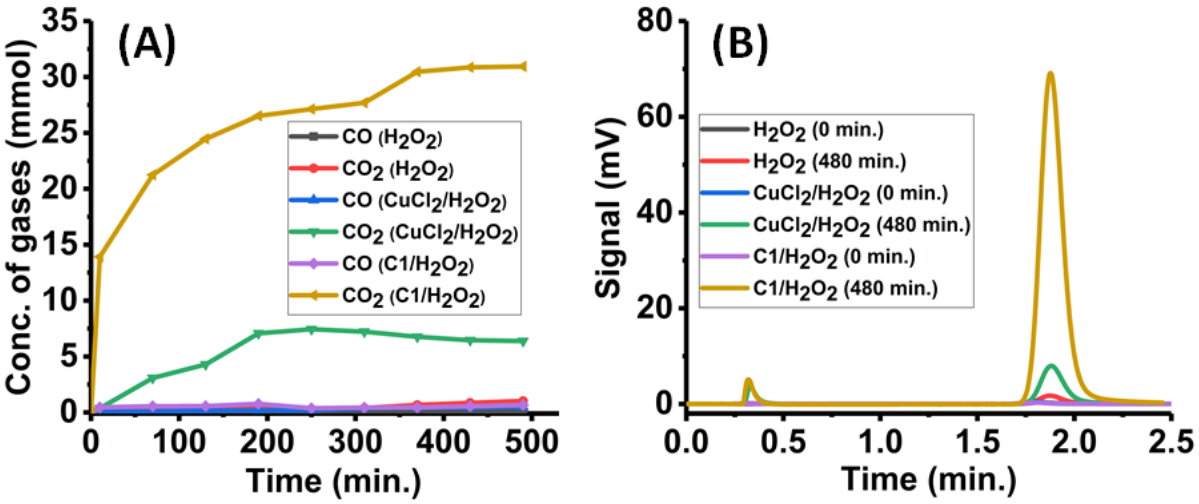


Figure S31. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of CR, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of CR. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

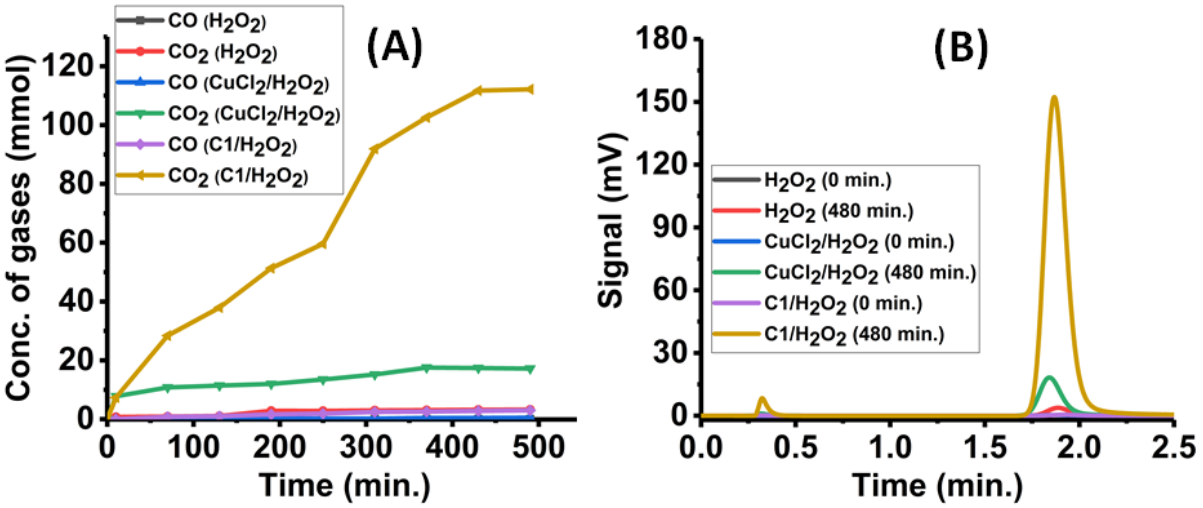


Figure S32. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of DB-71, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of DB-71. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

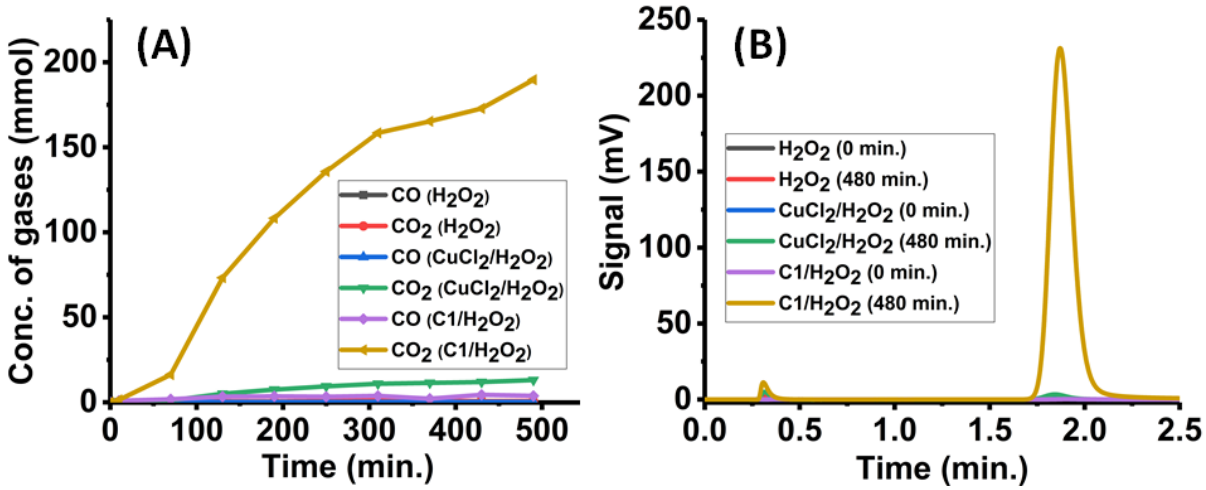


Figure S33. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of FS, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of FS. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

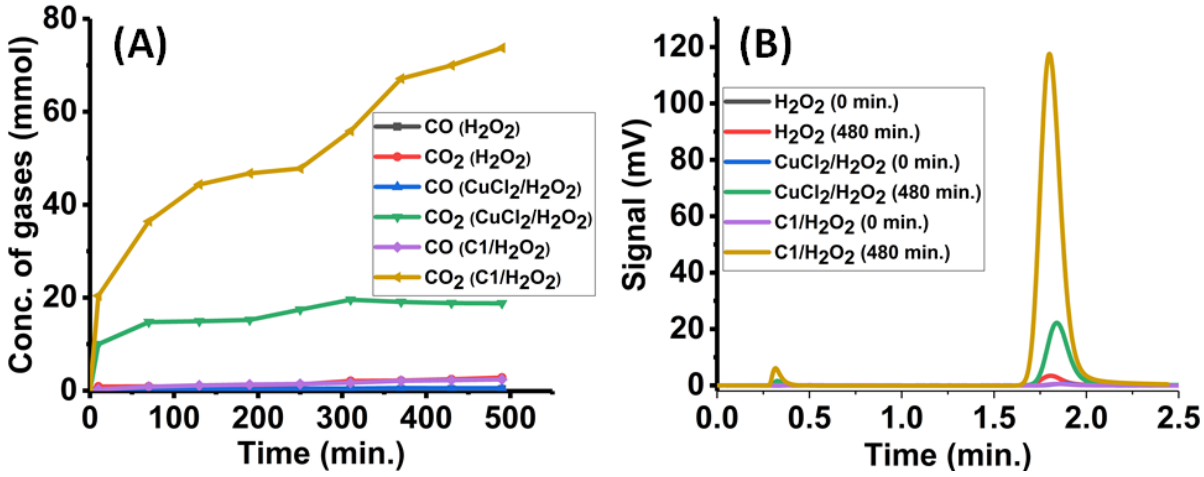


Figure S34. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of IC, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of IC. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

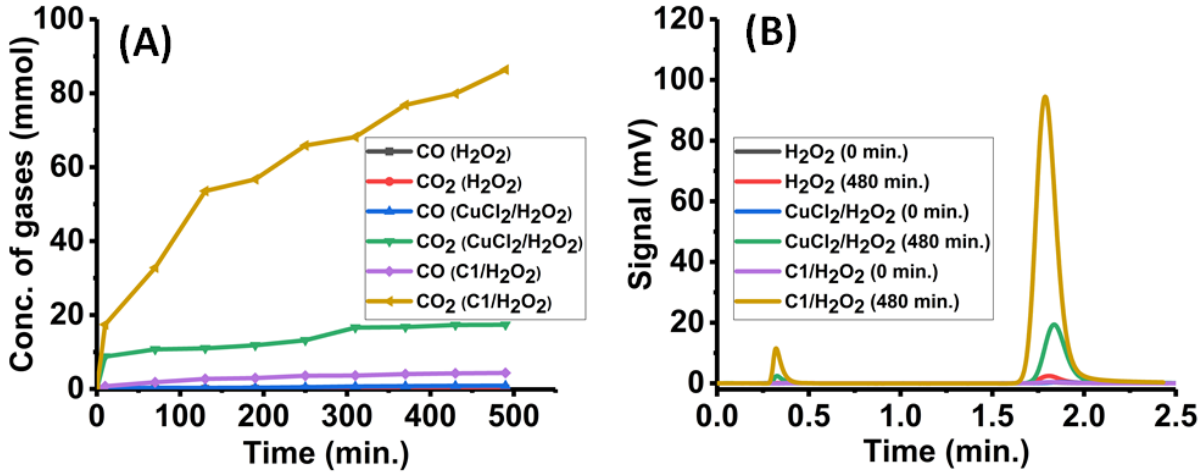


Figure S35. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of MBH, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of MBH. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

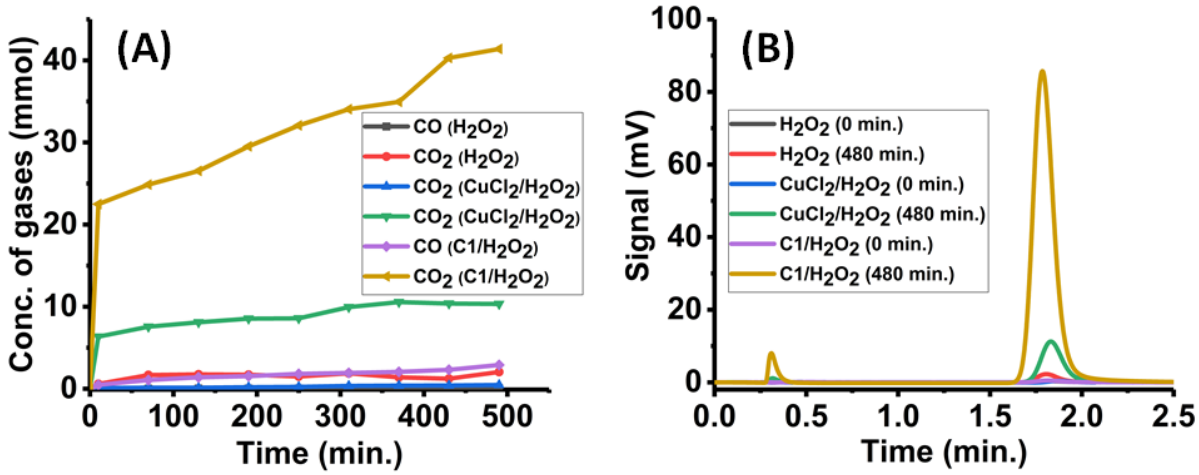


Figure S36. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of MO, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of MO. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

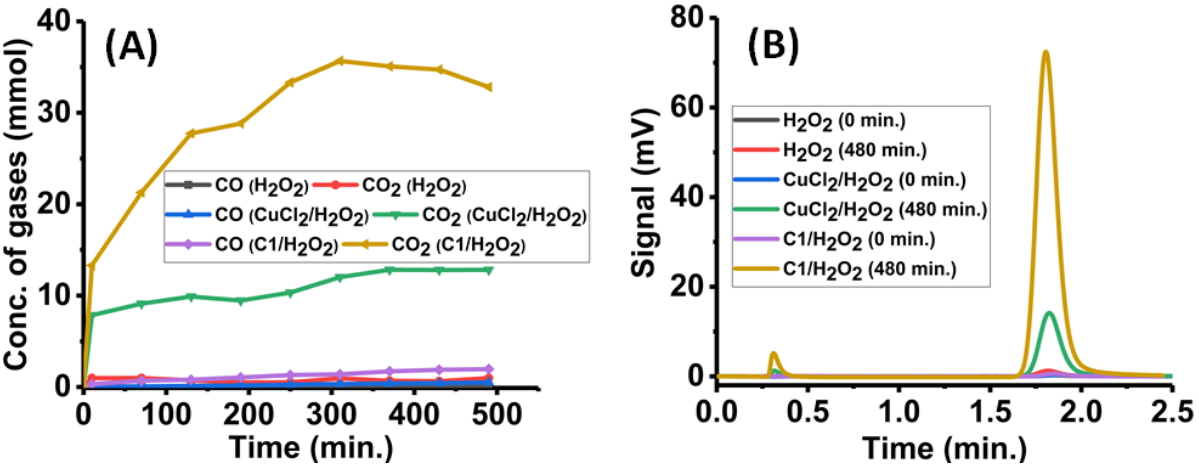


Figure S37. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of MR, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of MR. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

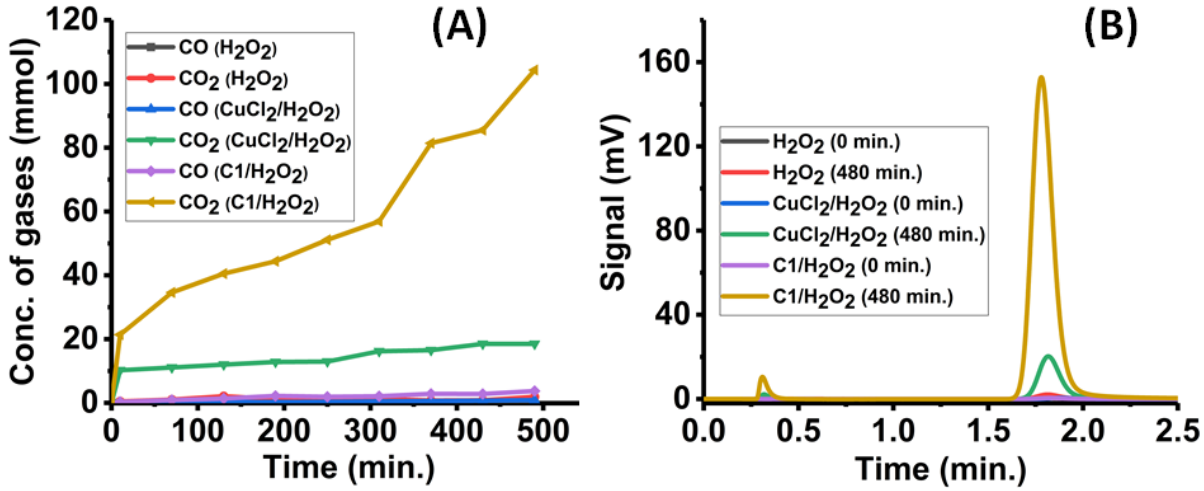


Figure S38. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of RB-5, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of RB-5. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

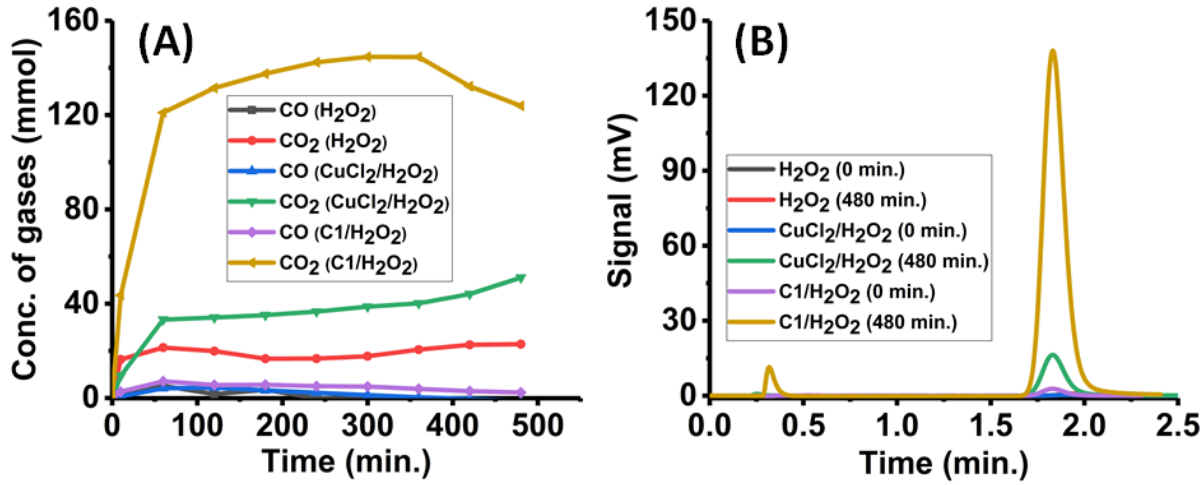


Figure S39. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of DE-1, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of DE-1. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

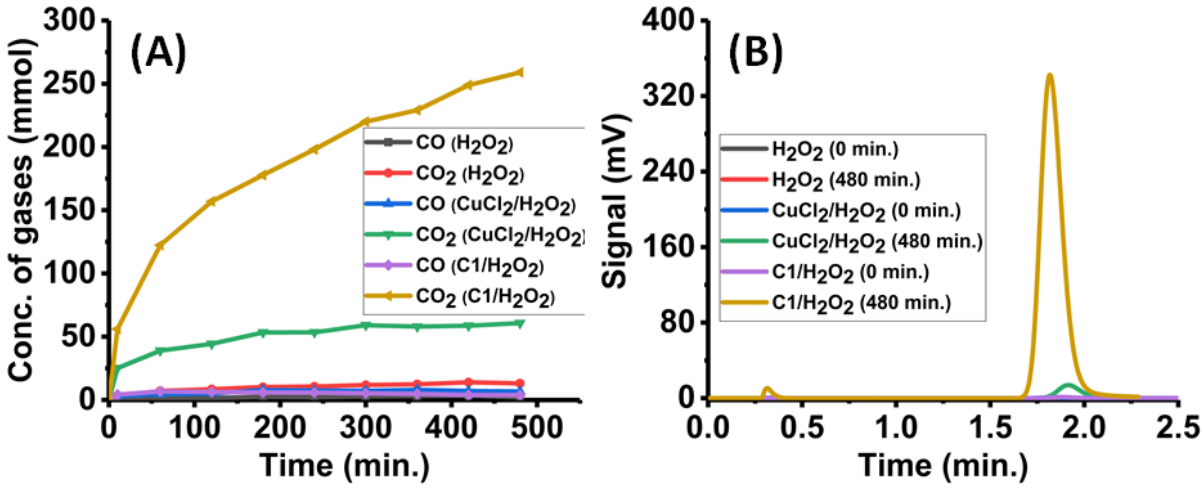


Figure S40. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of DE-2, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of DE-2. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

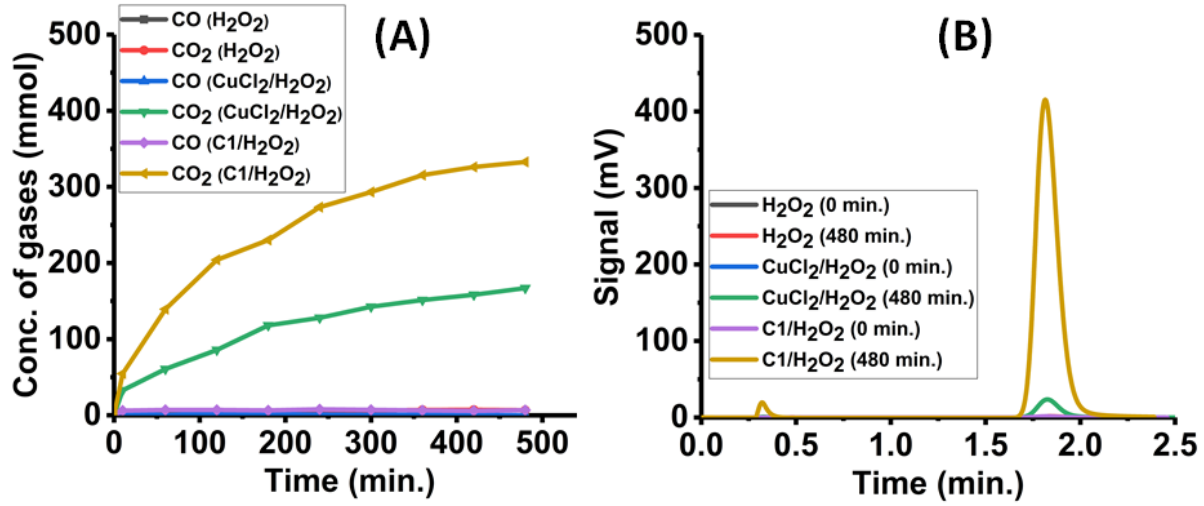


Figure S41. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of DE-3, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of DE-3. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

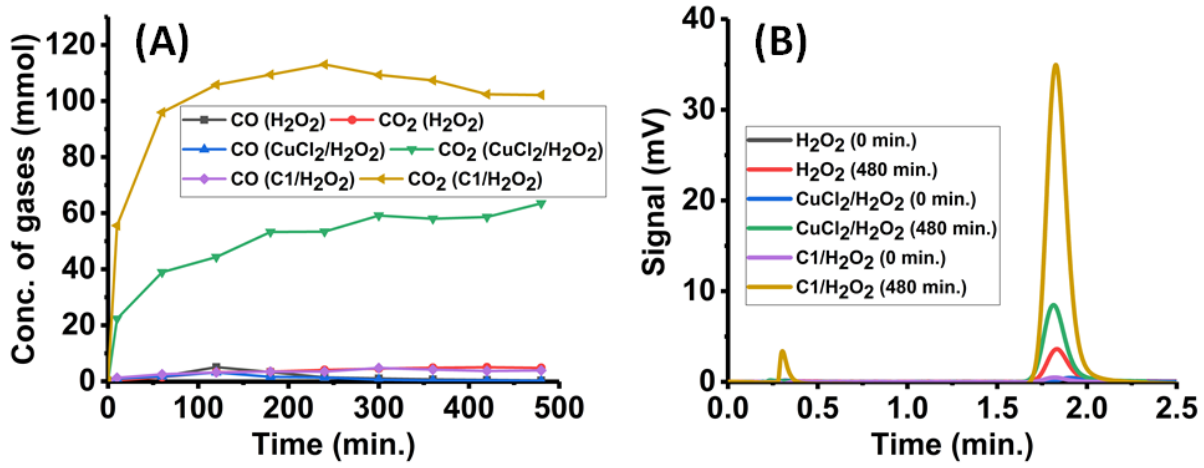


Figure S42. (A) The Concentration of CO_2 and CO calculated after 8 hrs treatment of DE-4, black trace for CO gas (H_2O_2), red trace for CO_2 gas (H_2O_2), blue trace for CO gas ($CuCl_2/H_2O_2$), green trace for CO_2 gas ($CuCl_2/H_2O_2$), violet trace for CO gas ($C1/H_2O_2$) and light yellow trace for CO_2 gas ($C1/H_2O_2$) (B) GC chromatogram obtained for CO_2 and CO after 8 hrs treatment of DE-4. Black, blue and violet trace recorded before treatment at 0 min in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively. Red, green and light yellow trace recorded after treatment at 8 hrs in presence of H_2O_2, $CuCl_2/H_2O_2$ and $CuCl_2/H_2O_2$ respectively.

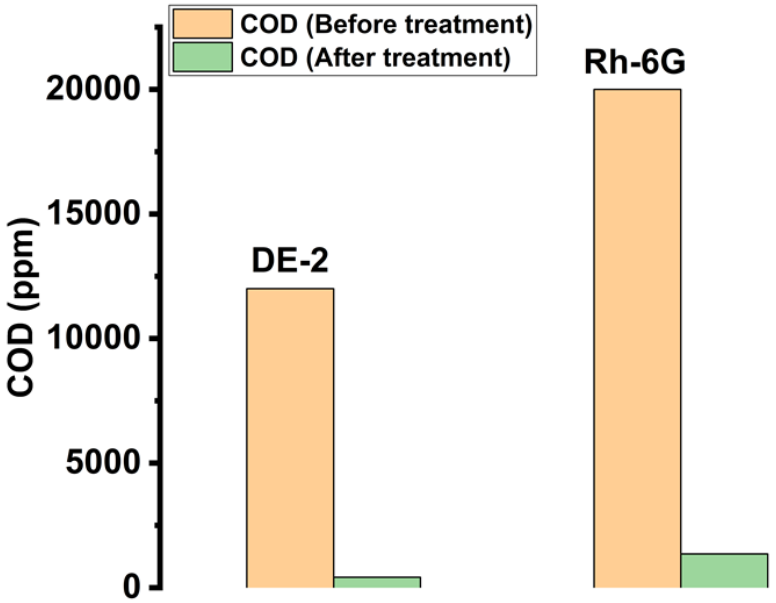


Figure 43. COD (Chemical Oxygen Demand) measured for DE-2 and Rh-6G before and after pre-treatment. COD results of dyes DE-2 and Rh-6G after 2 hrs. and 8 hrs. respectively. After treatment, COD has decreased up to 95-98 % in the case of all dyes.

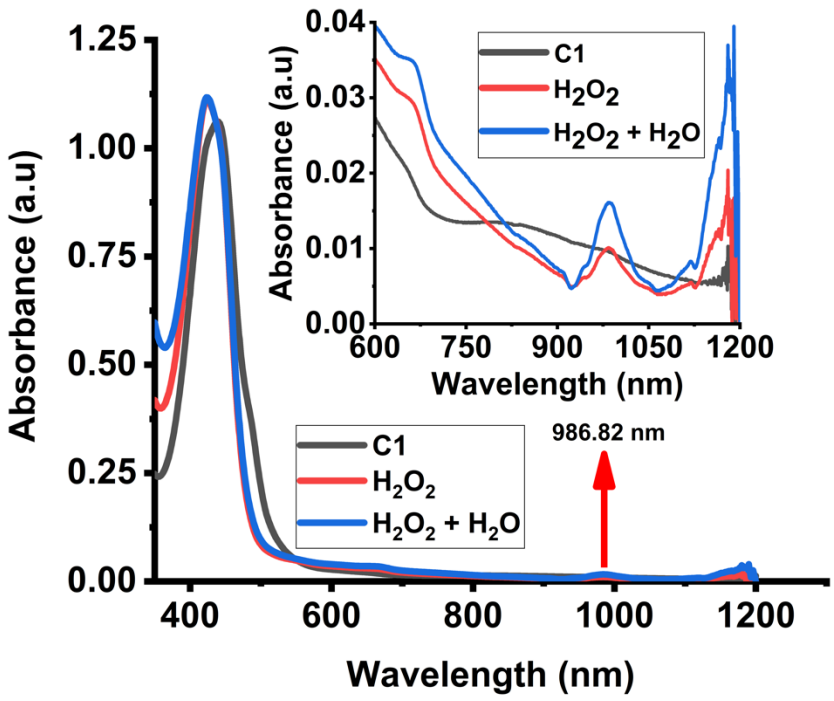


Figure S44. Optical spectra recorded for C1 (1 mM) in DMF by addition of 60 µl of H_2O_2 and water respectively. C1 complex (black trace), C1 complex in presence of 60 µl of H_2O_2 (red trace) and C1 complex in presence 60 µl H_2O_2 and 60 µl of water. All data recorded at room temperature.

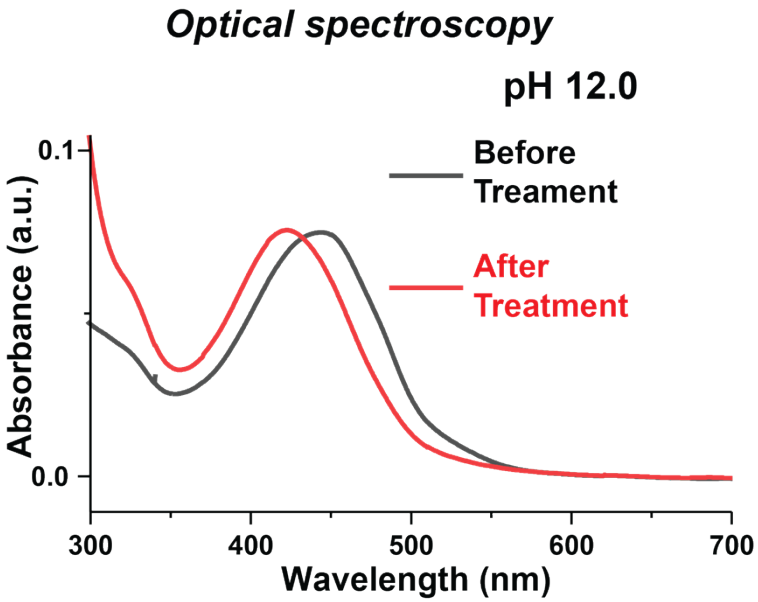


Figure S45. Optical spectra recorded for C1 (0.1 mM) in water (pH 12.0) before (black trace) and after (red trace) the dye treatment studies. All data recorded at room temperature.

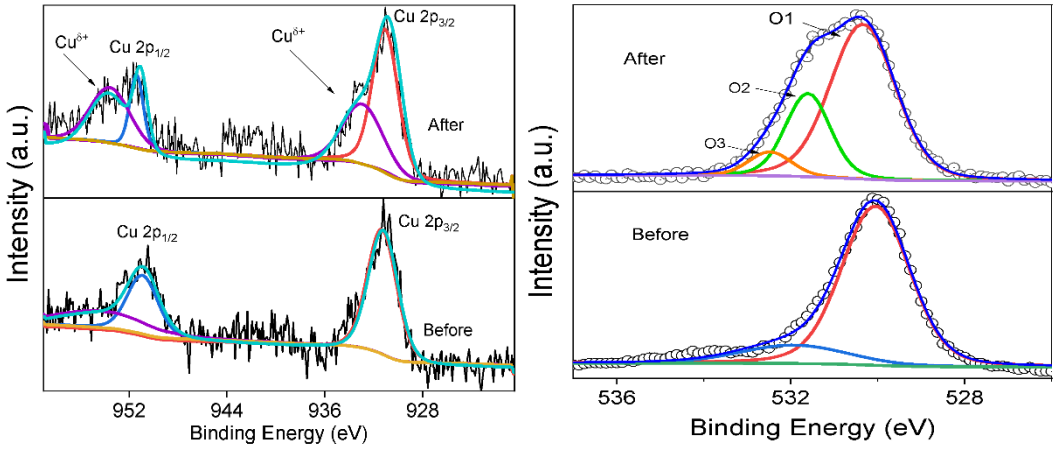


Figure S46. The XPS spectra recorded for Cu2p (left) and O1s (right) region before and after the dye treatment. The raw data is represented in black trace, while the convoluted data is shown in colred traces.

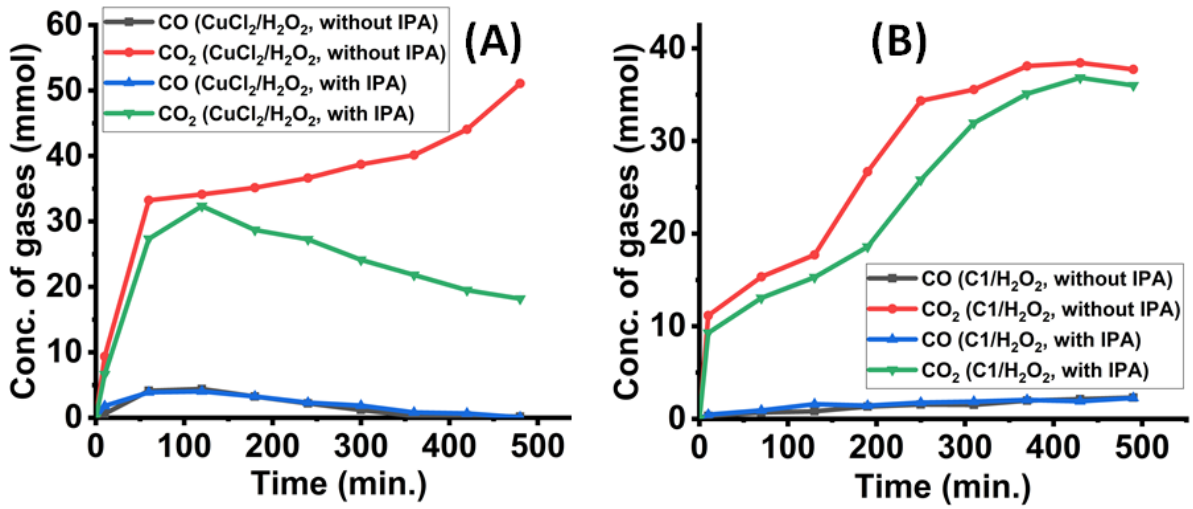


Figure S47. (A) The concentration of CO_2 and CO calculated after 8 hrs treatment of DE-1 in presence of $CuCl_2/H_2O_2$ before the addition of IPA (isopropyl alcohol) and after addition of IPA (C1: IPA ratio, 1:100). black trace for CO gas in presence of $CuCl_2/H_2O_2$ absence of IPA, red trace for CO_2 gas in presence of $CuCl_2/H_2O_2$ and absence of IPA, blue trace for CO in presence of $CuCl_2/H_2O_2$ and IPA, green trace for CO_2 in presence of $CuCl_2/H_2O_2$ and IPA. (B) The concentration of CO_2 and CO calculated after 8 hrs treatment of Rh-6G in presence of $C1/H_2O_2$ before the addition of IPA (isopropyl alcohol) and after addition of IPA (C1: IPA ratio, 1:100). black trace for CO gas in presence of $C1/H_2O_2$ absence of IPA, red trace for CO_2 gas in presence of $C1/H_2O_2$ and absence of IPA, blue trace for CO in presence of $C1/H_2O_2$ and IPA, green trace for CO_2 in presence of $C1/H_2O_2$ and IPA.

Table S1. Percentage degradation of standard dyes and industrial effluent in presence of different analysts (H_2O_2, $CuCl_2/H_2O_2$, and **C1**/H_2O_2) at room temperature and pH 7.0.

S. No.	Name of dyes	Percentage Degradation after treated with H_2O_2	Percentage Degradation after treated with $CuCl_2/H_2O_2$	Percentage Degradation after treated with $C1/H_2O_2$	Degradation time
1.	Amido Black (AB-10B)	6.30	56.80	96.84	80 min
2.	Brilliant Blue G (BBG)	15.00	50.00	98.50	6 hrs
3.	Brilliant green (BG)	36.45	45.83	96.33	4 hrs
4.	Carmine (CR)	8.00	62.80	100	1 hr
5.	Direct Blue-71 (DB-71)	2.00	9.00	100	1 hr
6.	Fluorescein (FS)	11.70	21.70	99.50	1 hr
7.	Indigo Carmine (IC)	24.00	54.00	100	30 min
8.	Methylene Blue Hydrate (MBH)	11.20	18.20	97.30	8 hrs
9.	Methyl Orange (MO)	20.25	29.70	100	2 hrs
10	Methyl Red (MR)	6.00	19.60	100	30 min
11	Reactive Black-5 (RB-5)	4.90	34.50	98.70	3 hrs
12	Rhodamine 6G (Rh-6G)	5.00	10.00	94.00	8 hrs
13	Dye effluent-1 (DE-1)	8.20	22.50	100	20 min
14	Dye effluent-2 (DE-2)	11.20	22.04	100	2 hrs
15	Dye effluent-3 (DE-3)	6.50	34.50	100	2 hrs
16	Dye effluent-4 (DE-4)	3.50	23.25	100	20 min

Table S2. Change in water quality parameters before and after the two-stage dye treatment

Parameters	DE-1		DE-2		DE-3	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
pH	12.84	8.3	10.10	8.46	12.31	8.6
TDS (mg/l)	3500	2530	6770	5400	6000	5400
COD (mg/l)	2150	< 100	4500	<250	2150	<250
Electrical Conductivity (mS/cm)	10.74	8.95	11.50	10.50	10.74	8.95
Color	Dark blue	Colorless	Dark green	Colorless	Dark bluish green	Colorless

Reference

(1) Ali, A.; Prakash, D.; Majumder, P.; Ghosh, S.; Dutta, A. Flexible Ligand in a Molecular Cu Electrocatalyst Unfurls Bidirectional O2/H2O Conversion in Water. *ACS Catal.* **2021**, *11* (10), 5934–5941. https://doi.org/10.1021/acscatal.1c01542.