# *Green synthesis of cubic CuO nanoparticles for biomedical applications and photodegradation of methylene blue: RSM-BBD optimization of reaction parameters, and stability studies*

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**Figure S1.** *C. macrocarpa* fruit

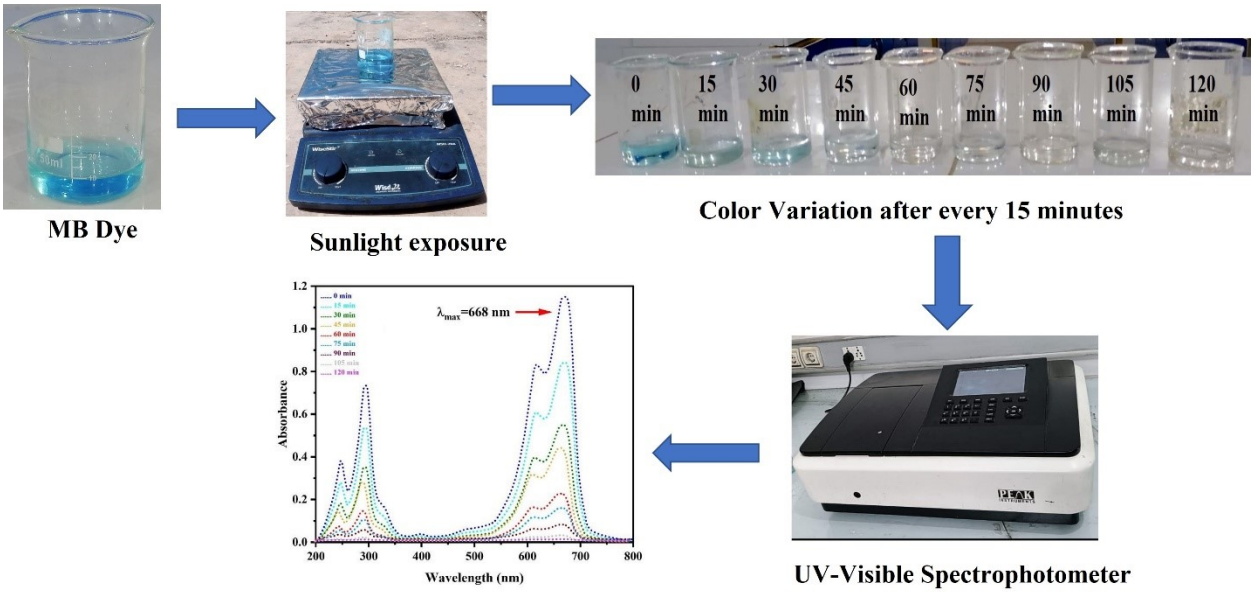


**Figure S2.** Scheme of photocatalytic activity analysis

**Table S1.** Details of variables and their coded levels

| Independent Variable (unit) | Symbol | Coded levels | | Mean |
|---|---|---|---|---|
| | | Low (-1) | High (+1) | |
| pH | A | 3 | 13 | 8 |
| Temperature (K) | B | 298 | 358 | 328 |
| Initial Concentration of pollutants (ppm) | C | 10 | 30 | 20 |
| Catalyst Dosage (mg) | D | 10 | 50 | 30 |

**Table S2**. Phytochemical screening results for the CMFE extract.

| Metabolite | Test | Observation | Result |
|---|---|---|---|
| **Phenols** | Lead acetate test | White precipitates | Positive |
| **Carbohydrates** | Molisch test | violet ring | Positive |
| **Tannins** | Braymer's Reagent test | greenish black color | Positive |
| **Flavonoids** | Shinoda test | pink scarlet color | Positive |
| **Terpenoids** | Salkowski test | pink scarlet color | Positive |
| **Saponins** | Foam test | Stable foam | Positive |
| **Anthraquinones** | Borntrager test | pink color | Positive |

| | | | |
|---|---|---|---|
| **Alkaloids** | Draggendorff test | Brown color | Positive |

**S1. Calculation of crystal parameters by XRD spectrum**

The Debye-Scherrer relation (**Equation a**), the dislocation density (δ) formula (**Equation b**), the micro strain formula (**Equation c**) and degree of crystallinity (**Equation d**) were used to compute the crystal parameters, which include crystallite size, dislocation density, micro strain and degree of crystallinity, respectively [30]. The values of these parameters are depicted in **Table 2**.

$$D = \frac{k\lambda}{\beta \mathrm{Cos}\,\theta} \qquad (a)$$

$$\delta = \frac{1}{D^2} \qquad (b)$$

$$\varepsilon = \frac{\beta}{4\tan\theta} \qquad (c)$$

$$Degree\,of\ Crystallinity = \frac{Area\,of\ crystalline\ peaks}{Area\,of\ all\ peaks} \times 100 \qquad (d)$$

Where 'D' is the crystallite size, 'K' is Scherer constant, 'λ' wavelength of X-rays, 'θ' is the diffraction angle and 'β' refers to the correspond to the FWHM.

**Table S3.** Fit summary of model by software for MB degradation

| Source | Sequential p-value | Lack of Fit p-value | Adjusted $R^2$ | Remarks |
|---|---|---|---|---|
| Linear | 0.4544 | 0.0008 | -0.0077 | |
| 2FI | 0.9986 | 0.0004 | -0.3148 | |

| | | | | |
|---|---|---|---|---|
| **Quadratic** | **< 0.0001** | **0.8471** | **0.9856** | **Suggested** |
| Cubic | 0.7013 | 0.7649 | 0.9824 | **Aliased** |

## S2. Butler-Ginley Equations

$$E_{CB} = X - E_C - 0.5E_g \quad (e)$$

$$E_{VB} = E_{CB} + E_g \quad (f)$$

Here, $X$, $E_C$ and $E_g$ are the Mulliken's electronegativity, the energy of free electrons (4.5 eV) and energy bandgap.

## S3. Proposed mechanism of MB degradation

The suitable mechanism of catalytic degradation of MB is represented by **Equations (g-o)**.

$$CuO + h\upsilon(UV - Vis) \rightarrow CuO(e^-(CB) + h^+(VB)) \quad (g)$$

$$H_2O(ads) + h^+(VB) \rightarrow OH^\bullet(ads) + H^+(ads) \quad (h)$$

$$O_2 + e^-(CB) \rightarrow O_2^{\bullet-}(ads) \quad (i)$$

$$O_2^{\bullet-}(ads) + H^+(ads) \; f \quad HOO^\bullet(ads) \quad (j)$$

$$HOO^\bullet(ads) \rightarrow H_2O_2(ads) + O_2 \quad (k)$$

$$H_2O_2(ads) \rightarrow 2OH^\bullet(ads) \quad (l)$$

$$MB + 2OH^\bullet \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O \quad (m)$$

$$MB + h^+(VB) \rightarrow \text{Oxidation Products} \quad (n)$$

$$MB + e^-(CB) \rightarrow \text{Reduction Products} \quad (o)$$

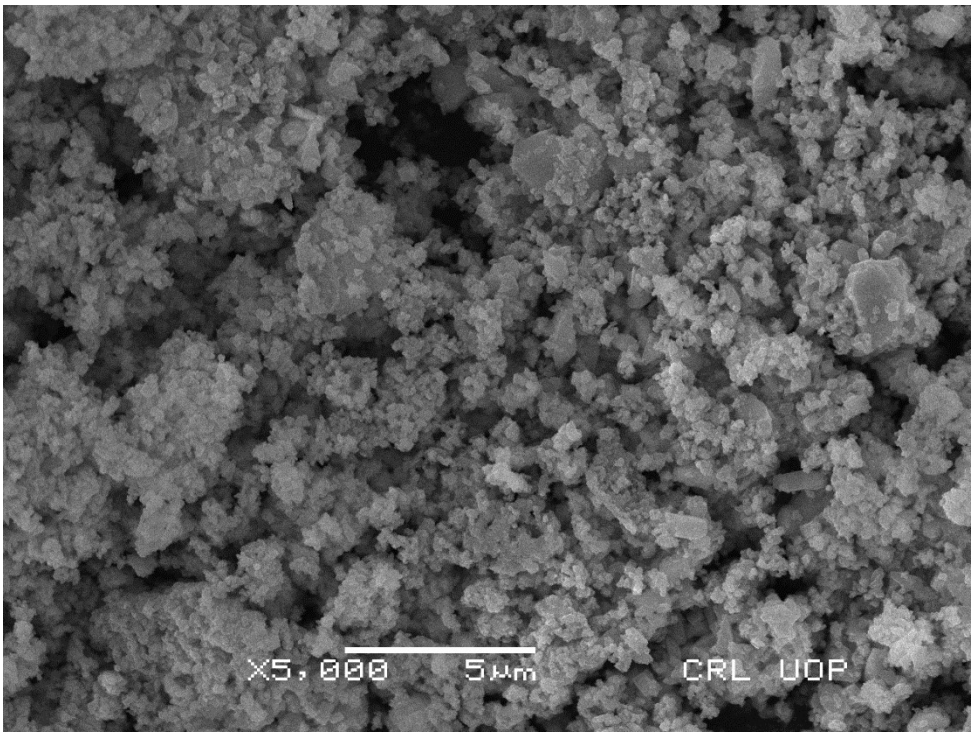


**Figure S3.** SEM image of CMFE@CuO NPs

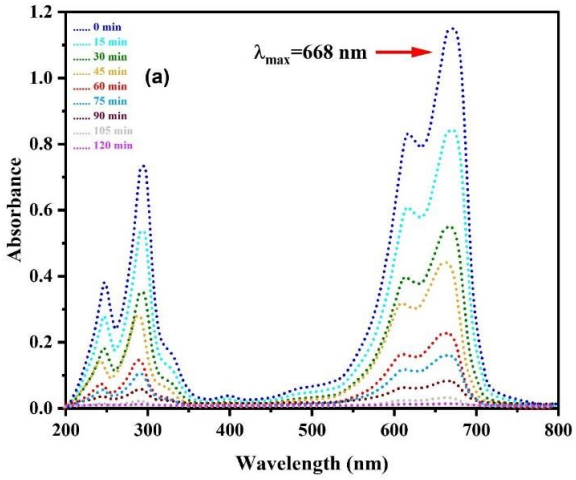


**Figure S4.** UV-Vis spectra of MB at different time intervals

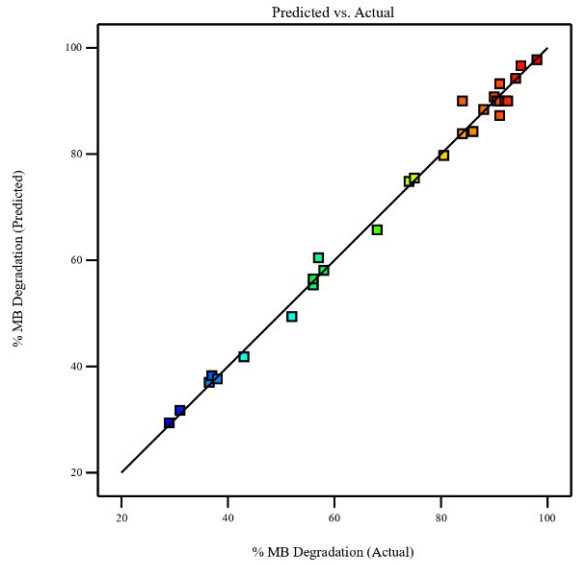


**Figure S5.** Actual values vs predicted values of MB dye degradation


**Figure S6.** Different resonance forms of MB dye

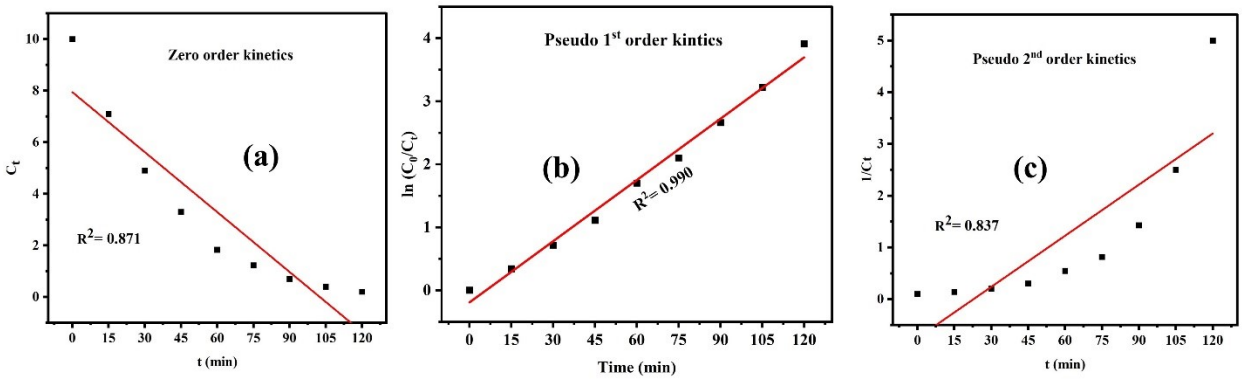


**Figure S7.** Data fitting of photodegradation of MB on CMFE@CuO NPs (a) zero-order kinetics, (b) Pseudo 1st order kinetics, and (c) Pseudo 2nd order kinetics

**Table S4.** Comparison table of different catalysts for photodegradation of MB

| Catalyst | Degradation (%) | Rate constant (k) ($min^{-1}$) | Reaction time (min) | Light source | Reference |
|---|---|---|---|---|---|
| Polythiophene doped ZnO | 80 | 0.0156 | 180 | 250 W high-pressure mercury lamp | [1] |
| CuO NPs | 97.5 | 0.0255 | 120 | UV light | [2] |
| Cu NPs | 90 | 0.0172 | 120 | sunlight | [3] |
| MgO NPs | 90 | 0.01544 | 120 | Xenon lamp (> 400 nm) | [4] |
| CuO/CuS/$MnO_2$ NCs | 98 | 0.022 | 160 | Visible light | [5] |
| $Zn_{0.5}Cu_{0.5}Fe_2O_4$ NPs | 94 | 0.026 | 135 | UV light | [6] |
| GO-$LaFeO_3$ NPs | 91.2 | 0.0137 | 150 | Visible light | [7] |
| CMFE@CuO NPs | 99.9 | 0.044 | 120 | sunlight | Current work |

## References


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