

Thermodynamic and kinetic study of synthesised graphene oxide-CuO nanocomposites: A way forward to fuel additive and photocatalytic potentials

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1 **Thermodynamic and kinetic study of synthesised graphene oxide-** 2 **CuO nanocomposites: A way forward to fuel additive and** 3 **photocatalytic potentials**

4
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21 **Abstract**

22 Rectangular shaped GO-CuO nanocomposites have gained special attention because of
23 spectacular applications in wastewater treatment. However, due to lack of research, the fuel
24 additive properties of GO-CuO are still unreported. A proper synthesis and characterisation
25 methods are necessary to investigate the fuel additive properties of GO-CuO. The present
26 research demonstrates the synthesis of graphene oxide (GO) sheets via a modified Hummers'
27 method. Further, GO-CuO nanohybrid was prepared by fast, cost-effective, and easy to handle
28 solvothermal approach. The crystal data such as crystal structure, unit cell parameters, space
29 groups, crystal system, and coordinates were explained via XRD analysis. Physical and
30 combustion properties of fuel were analysed at different concentrations (0, 20, 40, 60 and 80
31 ppm) of diesel-GO-CuO blend for fuel quality parameters. The flash point and fire point of
32 pure diesel oil were observed as 78 and 80 °C which were decreased to 50 and 58 °C respectively
33 at 80 ppm concentration. With GO-CuO nanocomposites the cloud point and pour point
34 decreases until a temperature of -8°C and -19 °C respectively with a pronounced decrease in

35 the viscosity up to 1.83 mm²/s. Further, the photocatalytic degradation of Methylene Red (MR)
36 dye is studied with the effect of changing H₂O₂, photocatalyst and dye concentrations with
37 time. Remarkably, the reaction kinetics and MR degradation of about 94% with sixth time
38 recyclability were observed. The results of this study showed improved MR degradation when
39 using GO-CuO with H₂O₂. GO-CuO applications can be utilised to remove other dyes in future
40 and to improve fuel quality parameters.

41 **Keywords:** Nanohybrid; Graphene oxide; Fuel additive; Photocatalysis; Crystal structure and
42 Photocatalytic potentials.

43

44 **1. Introduction**

45 Nowadays, fuel energy is the backbone of countries progress and mainstay of the automobile
46 industry. Recently, the issues such as; lavish fuel prices, depletion of crude oil resources, high
47 growth rate, low engine performances and elevated threats of global warming have been raised
48 throughout the world. These alarming circumstances necessitated focused research on fuel
49 quality, efficiency, and consumption improvements. The physicochemical properties of fuel
50 largely impact on diesel engine emissions and performance. Improved physicochemical
51 properties of diesel may lead to lower environmental pollution by decreasing unburned fuel
52 contents, hazardous gases and increased available energy contents from the fuel [1, 2]. In this
53 scenario, metal and organic oxides (ZnO, SnO, CuO, MnO, GO) based nanoparticles and
54 nanocomposites can improve physicochemical properties with the reduction in unburned
55 hydrocarbons (UHCs) and conversion of CO into greenhouse gas (CO₂) [3].

56

57 On the other side, industrialisation produce sources of dyes contaminated water and
58 continuously released hazardous waste, threatening environmental safety and living organisms.
59 Due to improper handling of synthetic and organic dyes from industrial wastewater, dyes could

60 easily be detected from watercolour [4]. About 7×10^5 tons of dyes are produced annually from
61 industries, and 15% dyes effluents are released in an open environment. The aromatic and azo
62 (-N=N-) structures of dyes are complicated for degradation due to their structural stability.
63 Biodegradation, membranes mechanism, coagulation, adsorption and photocatalysis are up to
64 date techniques used for industrial wastewater treatment of dyes (Methylene red, Brilliant
65 green, Congo red and Methylene blue) [5, 6]. Among the available techniques, photocatalytic
66 degradation is extensively used for dye removal due to low cost, inhibition of secondary
67 pollutants and removal of colour with complete degradation of organic pollutants.
68 Photocatalysis produces electron-hole pairs and initiates the photoreaction by generating OH
69 free radicals [7, 8].

70

71 Transition metal oxides such as; TiO₂, ZnO, SnO, Fe₂O₃, Al₂O₃, Co₂O₃ and CuO are used as
72 photocatalysts and fuel additives because of their high volume to size ratio, thermal
73 conductivity and surface area [9-13]. However, these metal oxides suffer high bandgap, low
74 quantum efficiency, toxicity, high electron-hole recombination, solar light inactivity and cost
75 inefficiency [14]. Among these CuO has high solar absorption with cost efficiency, nontoxicity,
76 photocatalytic and fuel additive properties [15, 16]. Although CuO has less photocatalytic
77 activity irrespective of low bandgap (1.2 eV), it is due to electron-hole recombination and
78 separation resistance after photocatalysis. This defect can be improved by combining CuO
79 nanoparticles with materials having electron-accepting and magnetically separable properties
80 [17-19]. It has been discovered that mixing of semi-porous zeolites, silica, alumina and carbon-
81 containing material like co-adsorbent with a metal photocatalyst, produced improved
82 photocatalytic hybrids. GO as an excellent material has a high oxygen and electrons availability
83 with electron transfer ability showed improved photocatalytic and exceptional magnetically
84 separable properties [20]. GO-CuO exhibit quantum-kinetic properties in photocatalysis due to

85 large electronic bandgap which inhibit electron-hole recombination. Metal ions and organic
86 compounds bind with oxygen-carrying groups attached on the GO surface via electrostatic
87 interactions and chemical coordination [21]. On the other side oxygen-carrying, a functional
88 group in GO increases the distance between hydrophilic carbon layers and oxidise fuels to
89 enhance its thermal properties. Hummers' method with some modifications is extensively used
90 to synthesise high oxygen content GO sheets [22].

91

92 Thus GO incorporated by transition metal (Co, Cu, Ni, and Fe) oxides display unique
93 synergistic properties. Variety of methods reported for the preparation of GO-CuO
94 nanocomposites such as noncovalent, wetness impregnation, covalent reaction, hydrothermal,
95 chemical electrolysis, solvothermal, electrophoresis, physical mixing and electrochemical
96 deposition. Hydrothermal and solvothermal methods attain superiority due to controlled size
97 and shape of nanostructure [23]. A very innovative study synthesised nanostructures of GO-
98 CuO and calculated their sensors catalytic ability for dopamine deficiency and biomedical
99 applications to kill microbes [24]. It has been studied that G-CuO nanocomposite has 4.84
100 times greater photocatalytic potential for MB dye as compared to CuO [25]. It has also been
101 studied that Cu₂O-RGO have 99% initial lithium-ion battery discharge for consecutive 25
102 cycles and Cu₂O behave as conversion electrode [26]. Graphene-based CuO nanocomposites
103 are extensively used as a photocatalyst, biomedical and lithium-ion batteries applications,
104 however, the best of our knowledge no research has been carried out yet on GO-CuO for the
105 fuel additive applications.

106

107 In contrast to previously reported studies, the need for this research work was to produce GO-
108 CuO nanocomposites for the diesel fuel quality enhancement and photocatalytic degradation
109 of MR organic dye. For this purpose, synthesised GO-CuO act as a diesel oil additive. To the

110 best of our knowledge, GO-CuO nanocomposites have never been implemented as a fuel
111 additive and organic dye degradation process at the same time. In this study, GO sheets were
112 prepared and anchored on the extensive surface of GO by solvothermal approach. Furthermore,
113 its applications to enhance the fuel quality mainly focusing on important fuel parameters such
114 as; fire point, flashpoint, cloud point, pour point, kinematic viscosity and specific gravity were
115 studied. MR was selected as dye pollutant for evaluating the dye degradation capability of GO-
116 CuO at optimum conditions of time, catalyst dose, H₂O₂ and dye concentration.

117

118 **2. Experimental**

119 **2.1 Chemicals**

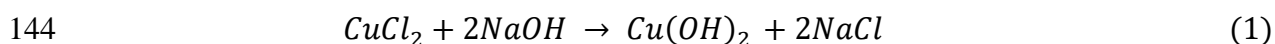
120 Graphite powder, sulphuric acid (H₂SO₄), sodium nitrate (NaNO₃) and potassium
121 permanganate (KMnO₄), copper chloride (CuCl₂ · 2H₂O), sodium hydroxide (NaOH), ethanol
122 (98%), and ethylene glycol were purchased from Sigma Aldrich (USA) and used as such
123 without further purification. De-ionised water (DI) was used in all synthesis methods.

124 **2.2 Preparation of GO-CuO nanocomposites**

125 GO sheets were synthesised via a modified Hummers' method [27]. First of all graphite powder
126 (3 g) and NaNO₃ (1.5 g) were dissolved in cold conc. H₂SO₄ (180 mL) and kept in an ice bath
127 with continuous stirring for 1 h. At this stage, fine powdered KMnO₄ (18 g) was added to
128 oxidise graphite with continuously mixing at 15 °C. The brownish-green solution was then
129 stirred without an ice bath for 2 days at 50 °C until it became thick brownish paste. After this,
130 distilled water (100 mL) was slowly dropped into the solution. In order to prevent oxidation,
131 30% H₂O₂ (60 mL) and distilled water (500 mL) were added to minimise the effect of KMnO₄.
132 Finally, thick brownish material was settled down and centrifuged at 3600 rpm with distilled
133 water to maintain a pH 7 of the given residues. In the end, the precipitates were dried in an
134 electric oven at 60 °C for 2 h to obtain fine GO sheets via a modified Hummers' method [28].

135

136 Eq. (1) illustrated the preparation of CuO nanoparticles via copper chloride (CuCl₂) as
137 precursor during the co-precipitation method [29]. At the first stage, CuCl₂.2H₂O salt (9 g) was
138 dissolved in ethanol (10 mL) and stirred for 40 min to prepared solution A. The solution B was
139 prepared via NaOH (5.4 g) mixing into ethanol (10 mL). Solution A and B gradually mixed
140 and kept on stirring. Stirring turned green solution to bluish-green and finally into thick black
141 CuO precipitates. Finally, centrifuged the mixture with distilled water to remove sodium
142 hydroxide impurities at pH 7. Then the sample was dried at 60 °C for 2 h and calcined at 500
143 °C for 5 h.



145

146 Following this, GO (0.6 g) sheets dispersed in ethylene glycol (20 mL) and stirred for 45 min
147 in a flask. A sample of CuO nanoparticles (2 g) stirred in ethylene glycol (20 mL) in another
148 container. Both solutions were mixed and sonicated together for 45 min. After complete mixing
149 with sonication, the material was added in Teflon lined autoclave and heated at 180 °C for 5 h
150 by following the solvothermal reaction as shown in Eq. (2).

151



153

154 After a given time, the mixture was cooled in an open environment and centrifuged at 3600
155 rpm with ethanol washing until pH 7 was obtained. The sample was dried at 50 °C for 4 h in
156 the oven following to calcination at 500 °C for 5 h. The schematic diagram of the synthesis
157 process is shown in **Fig. 1** [30]. The obtained product was ready for further applications.

158 **2.3 Characterisation**

159 The prepared CuO and GO-CuO were analysed via XPERT-PRO diffractometer with
160 minimum 0.001° scan step size and 2θ range of 10–80° to get XRD pattern. The amorphous

161 samples were dispersed at the substrate and used radiations of Cu-K α ($\lambda=1.5417$ nm) [31]. The
162 obtained results were analysed for lattice parameter calculations with the use of MATCH 3
163 software. Further, VESTA was used to construct structural models of metal oxide sample. The
164 CuO and GO-CuO having either morphology were identified at 9 kV power by the use of SEM
165 JEOL JSM-6480A. Double beam UV visible spectrophotometer was used to measure the
166 catalytic oxidation-reduction of MR organic dye. During the fuel additive application, APEX-
167 JCX309 Cleveland open cup tester was used to determining the flash point and fire point
168 values. APEX-JCX406 bomb calorimeter at GB/T213 standard was utilised to obtain the
169 calorific value of specific concentrations such as; 0, 20, 40, 60 and 80 ppm of diesel-GO-CuO
170 solutions. The viscosity of these solutions was measured by using ASTM D445 Ostwald
171 viscometer [32].

172 **2.4 Fuel additive and photocatalytic properties**

173 The physicochemical characteristics of diesel oil were studied at laboratory scale.
174 Characterisation of all properties was observed with the introduction of GO-CuO (0.002-0.008
175 mg) in 100 mL of commercial PSO diesel and prepared solutions of 20, 40, 60 and 80 ppm
176 concentrations. Their combustion analysis was estimated by flash point, fire point and calorific
177 values with the use of Cleveland open cup tester and Bomb calorimeter. Cleveland open cup
178 tester has an operating temperature range as 10 to 350 °C. On the other hand, physical
179 characteristics of these different dispersions were studied by kinematic viscosity, specific
180 gravity, cloud point and pour point with the assistant of Ostwald viscometer, gravity meter and
181 digital thermometer respectively [33]. The comparison between the results of different
182 solutions for flash point, fire point, calorimetric values, cloud point, pour point, specific gravity
183 and kinematic viscosity values are presented in **Table 1**.

184

185 The photocatalytic degradation of MR was investigated via UV-visible spectrophotometer at
186 200–800 nm wavelength range. The experiment was performed at constant temperature (35
187 °C), and at pH 8 with 1.5 M H₂O₂ added in 20 ppm dye solution in a beaker. Then 0.35 mg
188 photocatalyst was added and kept the solution in a dark environment for 2 h to achieve the
189 adsorption-desorption equilibrium, respectively. Later on, 3 mL of aliquot was collected step
190 by step after a continuous interval of time and absorbance spectra were measured under a
191 controlled environment of the spectrophotometer. The intensity of spectrophotometer was
192 adjusted at $\lambda_{\max} = 510$ nm of MR [34]. Finally, the equilibrium adsorption capacity was
193 calculated following the Eq. (3):

$$194 \quad qe = (C_o - C_e)V/W \quad (3)$$

195
196 where C_o is initial dye concentration in ppm, C_e is equilibrium dye concentration in ppm, V is
197 the volume of dye solution, and W is adsorbent mass in mg. Finally, the removal percentage
198 was determined by using Eq. (4):

$$199 \quad \% \text{ Removal} = (C_o - C_e)/C_o \times 100 \quad (4)$$

200
201
202 The rate of dye removal was investigated with different concentration of H₂O₂ (1–3 mL),
203 photocatalyst samples (GO, CuO and GO-CuO), specific concentrations (0.20, 0.25, 0.30 and
204 0.35 mg) of GO-CuO and dyes solutions (20, 30 and 40 ppm) at variable time duration from 0
205 to 90 min [35].

206 **3. Results and discussion**

207 **3.1 Structural and morphological analysis**

208 The crystal structure of GO is explained by XRD pattern and presented in **Fig. 2** (a). GO has
209 2θ value implies at 10.98° belongs to (001) plane. The XRD pattern of CuO has 2θ as 35.60° ,

210 38.90, 48.65, 61.7 and 68.16° corresponding to lattice planes as (002), (111), (220), (111) and
211 (113) respectively with JCPDS number 96-901-6327 as shown in **Fig. 2** (b). The observed
212 dimensions indicate that given CuO diffraction pattern have a monoclinic lattice structure [36].
213 Further, **Fig. 2** (b) illustrates the diffraction peaks of GO-CuO with 2θ values in the series of
214 23.20, 32.50, 35.47, 38.70 and 46.20° with corresponding crystallographic plane values of
215 (020), (110), (002), (111) and (-112) respectively with JCPDS numbers 96-901-5925. It
216 confirms that after solvothermal, the (001) plane of GO peak with $2\theta=10.98^\circ$ has shifted to
217 (020) plane in GO-CuO due to the reaction of GO with CuO metal nanoparticles. It has also
218 been observed that GO and CuO structures have not been destroyed after their chemical
219 combinations and agreed well with already reported planes (002) (200) and (113) for
220 monoclinic CuO-RGO [35]. On the other hand, (110) plane have a high-intensity peak as
221 compared to previous studies due to the use of GO without further reduction or some type of
222 moisture contents.

223

224 There is no extra peak due to low noise ratio values. Moreover, the XRD pattern shows that
225 the sample of nanoparticles has pure and sharp peaks, that specifies the sample is highly
226 crystalline. Space groups, unit cell parameters, coordinates and density of CuO are explained
227 in **Table 2**. The study of diffraction peaks illustrated that CuO has a monoclinic structure with
228 $C1\ 2/c1$ (15) space group [37]. One Cu atom bonded with four oxygen atom in tetrahedral
229 position and there are 22 total atoms in on unit cell as shown in **Fig. 3** (a-b) with standard
230 atomic colours. Unit cell shows complex bonding arrangements with unique axis b in **Fig. 3**
231 (c). One unit cell possesses six polyhedral planes, out of which four planes are shared with
232 another unit cell as shown in **Fig. 3** (d). While **Fig. 3** (e-g) represents the orientation of (002),
233 (111) and (220) respective plans. **Fig. 3** (h) shows all the possible lattice planes present in CuO

234 as (111), (002), (220) and (113) successfully in one unit cell. It is observed that all the
235 crystallographic planes pass through at least two polyhedral planes.

236

237 The morphological studies were carried out via SEM analysis of CuO and GO-CuO after
238 calcination at 500 °C and represented in **Fig. 4** (a-d). The SEM images were collected at
239 different magnifications such as 100, 250, 500 and 800× with viewing ranges of 50-500 μm. It
240 has been revealed that CuO is in rectangular shaped particles having a high rate of aggregation
241 with each other and form dispersed rectangular-shaped arrangements to lower their surface
242 energies. The particles surfaces are rough from outside and become finer towards inwards. **Fig.**
243 **4(e-h)** illustrated highly dispersed CuO nanoparticles on the GO sheets and showed particles
244 as sheet-like morphology. It can be identified that GO has amorphous structural morphology
245 on which CuO nanoparticles are evenly distributed. These CuO nanoparticles are highly
246 stacked on graphene sheets that prevent their agglomeration and stacking with each other. The
247 observed results can also be justified well by the same trend of agglomerated nanoparticles on
248 graphene sheets in Cu₂O/RGO [38].

249 **3.2 Nanocomposite as a fuel additive**

250 The flash point and fire point were determined to find out the combustion properties of diesel
251 oil. Flash point is the lowest temperature at which a liquid starts to ignite in contact with air.
252 While the fire point is the lowest value of temperature at which mixture a fuel starts burning
253 [39]. Solutions of different concentrations (0, 20, 40, 60 and 80 ppm) are presented in **Fig. 5**
254 (a) after flash point and fire point analysis. The reference solution has no concentration of GO-
255 CuO, so displayed high-temperature values for flash and fire points. The reference values for
256 flash and fire point were 78°C and 80°C, respectively. As the concentration of GO-CuO
257 increased up to 40 ppm, the values of flash point decreased from 78 to 66 °C. On the other side,
258 the decreasing trend for fire point was 80 to 69 °C at 40 ppm concentration gradient. This

259 lowering temperature value indicates that GO-CuO is an excellent fuel catalyst and has the
260 characteristics effect to enhance the combustion rate of diesel oil in short duration with delayed
261 ignition.

262

263 Furthermore, GO-CuO show enhanced surface area and capability to increase the heat of
264 evaporation of nanocomposite diesel blend. As a result, it catches combustion fire more
265 quickly. Secondly, the high oxygen content of nanocomposite as a structural oxidiser, attribute
266 high thermal conductivity by decreasing evaporation time and efficiently oxidises SO (sulphur
267 oxide) and CO (carbon monoxide) into SO₂ and CO₂ during fuel combustion. In this way
268 decreases the flash point, fire point and lower the environmental threat of pollutant gases.
269 Zubair *et al.* [40] also studied the diesel oil for flash point and fire point with the assistance of
270 rGO-ZrO₂ as a fuel additive. It was reported that rGO-ZrO₂ reduced the flash point and fire
271 point values up to 52 and 60 °C. Therefore, careful handling is required even at 40 ppm
272 concentration of the catalyst.

273

274 The present research reported the flash point and fire point at 40 ppm concentrated diesel blend
275 of GO-CuO as 66 and 69 °C respectively. These results are better as compared to the already
276 reported in the study of rGO-ZrO₂ [40]. **Fig. 5** (b) shows that the reference solution has attained
277 a cloud point at -4 °C and pour point at -14 °C. The cloud point decreased rapidly for 0–80 ppm
278 solutions up to -8 °C. The pour point was also measured for declared concentration (0–80 ppm)
279 and showed a gradual decrease from -14 to -19 °C. As the concentration of GO-CuO increases,
280 a noticeable change occurs in values of cloud point and pour point. It decreases the
281 intermolecular forces between the diesel molecules and as a result fuel showed restricted
282 fluidity even at -19 °C. These observations can also be compared with decreased cloud point (2
283 °C) and pour point (-13 °C) values as a result of rGO-ZrO₂.

284

285 Whereas the GO-CuO nanocomposite revealed high depression in cloud point and pour point
286 up to -8 and -19 °C respectively as compared to rGO-ZrO₂ [40]. Hence, GO-CuO may be used
287 in cold areas to inhibit the freezing of diesel oil in automobiles. The cloudy appearance of
288 diesel is due to wax crystals formation at low temperature that could reduce its combustion. In
289 GO-CuO treated fuel, benzene rings show no polarity and crystallised diesel oil alkanes. Thus,
290 increase their starting time of precipitation, modify crystal growth orientation and inhibit
291 crystallisation. The polar CuO groups on the graphene surface restrict the wax crystals growth.
292 Therefore, diesel fuel blended with GO-CuO easily moves through engines filter and presents
293 excellent flowing properties.

294

295 The specific gravity of GO-CuO nanocomposite in the diesel fuel was determined at 0, 20, 40,
296 60 and 80 ppm concentrations. It is observed that the GO-CuO in diesel has a constant value
297 of gravity. Different concentrations of GO-CuO were introduced in 100 mL of diesel oil. For
298 0 ppm solution, specific gravity was 8.27 g/cm³ that was increased to 8.91 g/cm³ at 40 ppm
299 additive blend. These observations can be compared with CaSn₃ as a diesel additive, which
300 reported the highest 8.55 g/cm³ specific gravity at 40 ppm concentration [41]. These differences
301 suggest that GO-CuO have higher gravity as compared to already reported fuel additive. When
302 the concentration gradient increased to 80 ppm, specific gravity also increased to 9.13 g/cm³.
303 Sample of zero GO-CuO concentration has less specific gravity as compared to the samples of
304 60 and 80 ppm diesel blends as clearly seen in **Fig. 5** (c).

305

306 Kinematic viscosity is the physical resistance of a mixture to flow at a specific temperature.
307 Different concentrations of GO-CuO analysed for diesel oil viscosity at 25 °C are illustrated in
308 **Fig. 5** (c). Flowing resistance decreased as GO-CuO concentration increases in diesel oil. As

309 the reference has no GO-CuO, therefore, showed much high viscosity as compared to 40 and
310 60 ppm GO-CuO-diesel blend. The reference solution with 0 ppm concentration of GO-CuO
311 has 1.93 mm²/s kinematic viscosity. However, 40 and 80 ppm diesel solutions have 1.85 and
312 1.83 mm²/s values for kinematic viscosity respectively. The observed kinematic viscosity for
313 CuO₂ (B20+100 ppm) and CaSn₃ as a fuel additive reported a pronounced increase as 4.71–
314 5.69 mm²/s and 2.68–3.30 mm²/s respectively with catalyst concentration. The previous studies
315 discussed this increasing trend with lubrication properties, however, GO-CuO showed
316 alternative results with optimum volatility and burning capacities [41, 42]. As an essential need
317 of low viscosity meets their benefits with cold conditions at 1.83 mm²/s for 80 ppm diesel
318 blend. It is an essential requirement of cold regions with enhanced capability of olefins to reach
319 towards the ignition chamber for combustion. Actually, GO-CuO particles decrease the
320 interlayer attraction between the diesel oil layers and increase the total available energy
321 contents of fuel during combustion [32].

322

323 Furthermore, 0, 20, 40, 60 and 80 ppm doses of diesel-GO-CuO were studied to measure the
324 calorific values with the assistance of bomb calorimeter. The GO-CuO-diesel mixture revealed
325 an increasing trend of calorific values with GO-CuO concentration. **Fig. 5** (d) shows a
326 continuous increase in calorimeter readings for a high concentration of nano additives in the
327 fuel. The observed calorific values for 0 and 20 ppm solutions of GO-CuO are measured as
328 43542 and 45304 J/g respectively. It is due to the reason that before reaching the combustion
329 chamber, heat contents became impoverished during the delayed ignition. After reaching to
330 ignition stage, oxygenated GO-CuO enhances the heat contents with a rapid rate of burning
331 and high calorific values were observed. Kalaimurugan *et al.* [42] studied the Neochloris
332 oleoabundans methyl ester (B20) blend with diesel for calorific values at different concentrated
333 solutions (25, 50, 75 and 100 ppm) of copper oxide. It is reported that B20 + 100 ppm blend

334 showed 45,519 J/g calorific measurements, whereas the synthesised GO-CuO increases the
335 calorific value up to 45,634 J/g at 80 ppm catalyst concentration even without B2O.

336 **3.3 Photocatalytic application of GO-CuO**

337 **3.3.1 Photodegradation of MR**

338 Methylene Red dye (MR) is a member of azobenzene dyes and realistically degrades at
339 ordinary sunlight conditions. MR has absorption maxima at $\lambda_{\max} = 510$ nm studied via
340 photocatalytic absorptions through UV-visible spectroscopic analysis. Degradation of MR
341 takes place due to oxidation with the photo catalytically generated free radicals [5]. The
342 photocatalytic degradation process is carried out with the assistance of H₂O₂ catalyst and UV-
343 visible light source. Initially, all prepared samples under photocatalytic conditions (30 mL of
344 20 ppm dye solution at pH 8 with GO-CuO = 0.35 mg) were studied. The absorbance of UV-
345 visible light decreases gradually with the passage of time and the maximum absorbance peak
346 was obtained at 510 nm as shown in **Fig. 6**.

347 **3.3.1 Comparative photocatalysis of GO, CuO and GO-CuO**

348 The photocatalytic degradation of MR was studied for GO, CuO and GO-CuO to compare the
349 photocatalytic behaviours. The experiment was conducted by keeping the same conditions for
350 all the parameters (concentration, temperature and pH). The GO-CuO represents 94% MR
351 removal efficiency as compared to GO and CuO. It is due to the extensively large surface area
352 of GO-CuO as compared to other photocatalysts. The comparative study follows the MR
353 degradation order as GO (78.9%) < CuO (85.5%) < GO-CuO (94%) in 90 min at pH 8, as shown
354 in **Fig. 7**. These results have a strong comparison to the already reported studies for degradation
355 of MR dye with the assistance of Ag@Fe, TiO₂-WO₃ and YMnO₃/CeO₂ composites. Ag@Fe
356 and TiO₂-WO₃ have 88 and 91% degradation ability in 100 and 120 min respectively. The
357 reported results showed that YMnO₃/CeO₂ can remove 99% MR dye, which has much-

358 improved photocatalysis but take 240 min. As compared to these results, GO-CuO degraded
359 about 94% MR dye in just 90 min [34, 43, 44].

360 **3.3.2 Effect of H₂O₂ on dye removal**

361 During photocatalysis, H₂O₂ in optimal concentration assist the degradation process as an
362 oxidising agent. Initially, light photons generate electron-hole pair and move electrons from
363 the valence band to conduction band of the photocatalyst. These photogenerated electrons
364 generate superoxide free radicals (OH) when reacting with surface oxygen and H₂O₂ molecules
365 to enhance the photodegradation. Different concentrations (1, 2 and 3 mL) of H₂O₂ were studied
366 with 0.35 mg GO-CuO for 20 mL dye solution at pH 8 to find the effect of H₂O₂ on percentage
367 removal of MR. **Fig. 8** illustrates plot of removal percentage versus time. It is observed that for
368 1 mL H₂O₂, removal percentage limited to only 40% even after 90 min. On the other hand, 3
369 mL H₂O₂ can remove about 94% MR at a contact time of 90 min. The removal efficiency order
370 of H₂O₂ appeared to follow as 1 mL < 2 mL < 3 mL respectively. These are the OH radicals in
371 H₂O₂ molecule that help in the dye degradation process and decrease the dye concentration in
372 industrial effluent.

373 **3.3.3 Effect of catalyst dose in photocatalysis**

374 Photocatalyst dosage is a critical point to observe the catalyst's capability for MR removal in
375 the current research. Increase in the concentration of photocatalyst reduces the absorption at a
376 low level and in turn, increases the degradation. To observe the suitable concentration of
377 photocatalyst, 0.20–0.35 mg dose of GO-CuO with 20 ppm concentration of MR along with
378 the addition of a constant amount of H₂O₂ (3 mL) at pH 8 was analysed. Rate of degradation at
379 0.20 mg dose of the photocatalyst was about 54%. However, the maximum catalytic amount
380 (0.35 mg) exhibited a high removal efficiency of 94% with a contact time of 90 min, as shown
381 in **Fig. 9**. It is due to the fact, a greater surface area of GO-CuO accommodates a large number
382 of MR molecules. Further increase in photocatalyst concentration shows no pronounced

383 increase in the degradation rate due to three main reasons; (1) combination of adsorbent
384 particles with dye molecules, (2) saturation of active sites and (3) agglomeration of
385 photocatalyst particles. However, it increases the absorption length of the paths diffusion. The
386 already reported results for the degradation of MR dye via Ag@Fe composite showed 93%
387 degradation for 56 mg/L concentration of catalyst [34]. While GO-CuO with 0.35 mg
388 concentration has 94% capability of MR dye removal.

389 **3.3.4 Effect of dye initial concentration**

390 **Fig.10** explains the effect of MR aqueous solutions of different concentration (20, 30 and 40
391 ppm) over GO-CuO under visible light at same conditions (0.35 mg photocatalyst, 3 mL H₂O₂
392 at pH 8). For the MR, at 20 ppm initial dye concentration, degradation capacity of GO-CuO
393 photocatalyst was determined as 94% with a contact time of 90 min. On the other side, as dye
394 concentration was increased up to 40 ppm, the removal capacity became limited to 50%. The
395 removal percentage follows decreasing order for dyes solutions as 20 ppm > 30 ppm > 40 ppm
396 at same irradiated time. In some cases, the effect of increasing concentration enhanced the
397 photocatalytic mechanisms of degradation. It is due to the availability of a large number of
398 active sites at the start of the reaction, which decreases over time due to blockage by the dye
399 molecules. It is observed that when dye molecules block all the active sites, the adsorption
400 capacity remains constant and a further increase in irritating time has no pronounced effect on
401 the degradation as reported in previous studies. The degradation of MR has also been reported
402 with different dye concentrations (66.30–90.20 mg/L) that showed 68% degradation at 66.30
403 mg/L of MR dye dosage [34].

404 **3.3.5 Adsorption kinetics models**

405 Pseudo-first-order kinetic model described the changes that occur in dye concentration with
406 time at equilibrium conditions. The mathematical expression for the model is given in Eq. (5)
407 [40]:

408
$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (5)$$

409

410 According to this model, q_t and q_e parameters represent the adsorption capacity in mg/g while
 411 k_1 is the pseudo-first-order rate constant in 1/L which can be determined by plotting $\log(q_e - q_t)$
 412 against time as shown in **Fig. 11** (a). Pseudo-second order kinetic model is extensively used to
 413 study the adsorption capacity of adsorbing material. It explains the mechanism of the process
 414 as long as the nanocomposite remains in contact with the dye solution. It can be represented by
 415 Eq. (6):

416
$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t \quad (6)$$

417

418 In pseudo-second-order differential equation, k_2 acts as the second-order rate constant in
 419 g/mg min and can be calculated by plotting t/q_t versus time scale as shown in **Fig. 11** (b) with
 420 determination coefficient (R^2) [40]. These models were applied to determine the kinetic
 421 parameters that were illustrated in **Table 3**. The pseudo-second-order kinetics parameters such
 422 as q_e , k_2 and R^2 were determined by following the kinetic Eq. (6). The intraparticle diffusion
 423 model is also studied for GO-CuO nanocomposite as represented in Eq. (7).

424
$$q_t = k_{id} \sqrt{t} + C \quad (7)$$

425

426 where q_t is the sorption capacity at time t , k_{id} is the rate constant for intraparticle diffusion and
 427 C represents the boundary thickness. The relationship can be plotted between q_t and \sqrt{t} that is
 428 illustrated in **Fig. 11** (c). The linear plot for pseudo-first-order represents the determination
 429 coefficient (R^2) values as 0.95, 0.47 and 0.43 for GO-CuO, GO and CuO, respectively. On the
 430 contrary, the pseudo-second-order linear equation plot for the same samples gives high R^2

431 values as 0.99, 0.71 and 0.98. Similarly, for the intraparticle diffusion model, these R^2 values
432 are; 0.97, 0.95 and 0.94. As the values related to q_e calculated, q_e experimental and rate constant
433 are also mentioned in **Table 3**. It can be determined that pseudo-first-order represents q_e
434 calculated value (0.23 mg/g) for GO-CuO with a vast variation from the experimental value
435 (34.98 mg/g) of q_e .

436

437 In the case of pseudo-second-order, q_e calculated (36.36 mg/g) value is comparable with q_e
438 experimental (34.98 mg/g). These results prove that adsorption of MR on the large surface of
439 GO-CuO does not follow the pseudo-first-order kinetic model. Further, the comparison of
440 determination coefficient R^2 proves the validity of pseudo-second-order model as compared to
441 pseudo-first-order. It indicates that dye removal from experimental solutions is due to
442 physicochemical interactions between adsorbent and dye solution. As illustrated in **Fig. 11** (d),
443 that adsorption capacities (q_e) of photocatalysts also vary from catalyst to catalyst. GO-CuO
444 nanocomposite represents large q_e and R^2 values as compared to CuO and GO photocatalysts.
445 GO-CuO also showed equal diffusion of MR particles around itself and bulk solution phase.
446 Therefore, GO-CuO efficiently used as photocatalyst by following the pseudo-second-order
447 kinetic model.

448

449 In the end, to determine the recyclability of GO-CuO, the recovery of the photocatalyst was
450 examined with the use of H_2O_2 . Fig. 12 shows about 94% removal of MR molecules
451 successfully up to the sixth run. Reusability yield decreases to 88% up to the eleventh run,
452 indicating the reliability of GO-CuO. It has been proved that CuO nanoparticles firmly attached
453 on the GO surface, so used up to eleven runs with 88% MR removal ability. Further reusability
454 decreases due to washing of catalyst with each run. The results show that GO-CuO is effective
455 photocatalyst and have reliability towards photocatalytic degradation of MR dye. Similar

456 trends have been observed for MR degradation with TiO₂-WO₃ (sulphated TW) and
457 YMnO₃/CeO₂ that showed 88 and 90% reliability up to only fifth and fourth cycle respectively
458 as compared to GO-CuO (94% up to the sixth cycle) [43, 44].

459

460 **4. Conclusions**

461 The solvothermal method was successfully applied to synthesise GO-CuO nanocomposites,
462 which acted as an efficient diesel additive and photocatalyst for MR removal. The structural
463 and morphological studies remarkably confirmed high crystallinity, synthesis of rectangular-
464 shaped binary nanocomposite and monoclinic crystal cell geometry. The XRD patterns for GO-
465 CuO give miller indices (020) (110), (002), (111) and (-112) respectively with 2θ values in the
466 series of 23.20, 32.50, 35.47, 38.70 and 46.20° respectively. The fuel additive utilisation
467 exhibited effective depression in flash and fire points up to 50 and 58 °C respectively, while in
468 fuel viscosity up to 1.83 mm²/s. Therefore, it increases the flowing property even at -19 °C and
469 effectively delayed the wax crystal formation with crystallisation modifications. Further, the
470 specific gravity reaches up to 9.13 g/cm³ at 80 ppm concentration of nanocomposite in 100 mL
471 diesel. The photocatalytic MR removal represents 94% capability of photocatalyst even at 0.35
472 mg concentration of GO-CuO for 90 min and successfully used up to the sixth run. It is due to
473 a short bandgap with an extensive surface area of GO-CuO and inhibition of electron-hole
474 recombination. GO-CuO as easy to prepare, cost-efficient and reusable photocatalyst that could
475 be applicable at industrial scale for the photocatalysis of other industrial dyes and fuel additive
476 applications.

477 **Acknowledgement**

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481 **References**

- 482 1. Uflyand, I.E., V.A. Zhinzhiro, and V.E. Burlakova, Metal-containing nanomaterials as
483 lubricant additives: State-of-the-art and future development. *Friction*, 2019. 7(2): p. 93-
484 116.
- 485 2. Hassan, M.H.A., et al., Kinetic and thermodynamic evaluation of effective combined
486 promoters for CO₂ hydrate formation. *Journal of Natural Gas Science and Engineering*,
487 2020: p. 103313.
- 488 3. Hoseini, S., et al., Performance and emission characteristics of a CI engine using
489 graphene oxide (GO) nano-particles additives in biodiesel-diesel blends. *Renewable*
490 *Energy*, 2020. 145: p. 458-465.
- 491 4. Liu, Y., et al., Rapid and high-efficiency removal of methylene blue onto low-cost
492 activated sludge: Role and significance of extracellular polymeric substances.
493 *Bioresource Technology Reports*, 2019. 7: p. 100240.
- 494 5. Waghmode, T.R., et al., Sequential photocatalysis and biological treatment for the
495 enhanced degradation of the persistent azo dye methyl red. *Journal of hazardous*
496 *materials*, 2019. 371: p. 115-122.
- 497 6. Sher, F., et al., Implications of advanced wastewater treatment: Electrocoagulation and
498 electroflocculation of effluent discharged from a wastewater treatment plant. *Journal of*
499 *Water Process Engineering*, 2020. 33: p. 101101.
- 500 7. Nuengmatcha, P., et al., Enhanced photocatalytic degradation of methylene blue using
501 Fe₂O₃/graphene/CuO nanocomposites under visible light. *Journal of Environmental*
502 *Chemical Engineering*, 2019. 7(6): p. 103438.
- 503 8. Güleç, F., F. Sher, and A. Karaduman, Catalytic performance of Cu-and Zr-modified
504 beta zeolite catalysts in the methylation of 2-methylnaphthalene. *Petroleum Science*,
505 2019. 16(1): p. 161-172.
- 506 9. Soudagar, M.E.M., et al., An investigation on the influence of aluminium oxide nano-
507 additive and honge oil methyl ester on engine performance, combustion and emission
508 characteristics. *Renewable Energy*, 2020. 146: p. 2291-2307.
- 509 10. Upadhyay, G.K., et al., Synthesis of ZnO: TiO₂ nanocomposites for photocatalyst
510 application in visible light. *Vacuum*, 2019. 160: p. 154-163.
- 511 11. Yang, W., et al., Graphene oxide-supported zinc cobalt oxides as effective cathode
512 catalysts for microbial fuel cell: High catalytic activity and inhibition of biofilm
513 formation. *Nano Energy*, 2019. 57: p. 811-819.
- 514 12. Magdalane, C.M., et al., Structural and morphological properties of Co₃O₄
515 nanostructures: Investigation of low temperature oxidation for photocatalytic
516 application for waste water treatment. *Surfaces and Interfaces*, 2019. 17: p. 100369.
- 517 13. Akika, F., et al., Structural and optical properties of Cu-doped ZnAl₂O₄ and its
518 application as photocatalyst for Cr (VI) reduction under sunlight. *Surfaces and*
519 *Interfaces*, 2020. 18: p. 100406.
- 520 14. Fodor, S., et al., Designed and controlled synthesis of visible light active copper (I)
521 oxide photocatalyst: From cubes towards the polyhedrons-with Cu nanoparticles.
522 *Applied Surface Science*, 2019. 484: p. 175-183.
- 523 15. Hajipour, P., et al., Chemical bath synthesis of CuO-GO-Ag nanocomposites with
524 enhanced antibacterial properties. *Journal of Alloys and Compounds*, 2020. 821: p.
525 153456.
- 526 16. Pratheepa, M.I. and M. Lawrence, Synthesis of CuO-Reduced Graphene Oxide
527 Nanocomposite for High Performance Electrochemical Capacitors. *International*
528 *Journal of Research*, 2018. 5(12): p. 4519-4424.

- 529 17. Sarkar, S., et al., Magnetic properties of graphite oxide and reduced graphene oxide.
530 *Physica E: Low-dimensional Systems and Nanostructures*, 2014. 64: p. 78-82.
- 531 18. Choi, J., et al., Preparation and characterization of graphene oxide supported Cu, Cu₂O,
532 and CuO nanocomposites and their high photocatalytic activity for organic dye
533 molecule. *Current Applied Physics*, 2017. 17(2): p. 137-145.
- 534 19. Zarren, G., B. Nisar, and F. Sher, Synthesis of anthraquinone based electroactive
535 polymers: A critical review. *Materials Today Sustainability*, 2019: p. 100019.
- 536 20. Kumar, R., et al., Self-assembled nanostructures of 3D hierarchical faceted-iron oxide
537 containing vertical carbon nanotubes on reduced graphene oxide hybrids for enhanced
538 electromagnetic interface shielding. *Composites Part B: Engineering*, 2019. 168: p. 66-
539 76.
- 540 21. Zaaba, N., et al., Synthesis of graphene oxide using modified hummers method: solvent
541 influence. *Procedia engineering*, 2017. 184: p. 469-477.
- 542 22. Wang, L., et al., Designed graphene-peptide nanocomposites for biosensor
543 applications: A review. *Analytica chimica acta*, 2017. 985: p. 24-40.
- 544 23. Smith, A.T., et al., Synthesis, properties, and applications of graphene oxide/reduced
545 graphene oxide and their nanocomposites. *Nano Materials Science*, 2019. 1(1): p. 31-
546 47.
- 547 24. Kumar, S.K., et al., Highly efficient multipurpose graphene oxide embedded with
548 copper oxide nanohybrid for electrochemical sensors and biomedical applications.
549 *Journal of Science: Advanced Materials and Devices*, 2017. 2(4): p. 493-500.
- 550 25. Darvishi, M., G. Mohseni-Asgerani, and J. Seyed-Yazdi, Simple microwave irradiation
551 procedure for the synthesis of CuO/Graphene hybrid composite with significant
552 photocatalytic enhancement. *Surfaces and Interfaces*, 2017. 7: p. 69-73.
- 553 26. Lu, Y., et al., One-Pot Synthesis of Cuprous Oxide-Reduced Graphene Oxide
554 Nanocomposite as an Anode Material for Lithium Ion Battery. *International Journal of*
555 *Electrochem Science*, 2017. 12: p. 3941-3949.
- 556 27. Ding, J., et al., Low-temperature preparation of magnetically separable Fe₃O₄@ CuO-
557 RGO core-shell heterojunctions for high-performance removal of organic dye under
558 visible light. *Journal of Alloys and Compounds*, 2016. 688: p. 649-656.
- 559 28. Gong, S., et al., Learning from nature: constructing high performance graphene-based
560 nanocomposites. *Materials Today*, 2017. 20(4): p. 210-219.
- 561 29. Phiwdang, K., et al., Synthesis of CuO nanoparticles by precipitation method using
562 different precursors. *Energy Procedia*, 2013. 34: p. 740-745.
- 563 30. Sakthivel, B. and G. Nammalvar, Selective ammonia sensor based on copper
564 oxide/reduced graphene oxide nanocomposite. *Journal of Alloys and Compounds*,
565 2019. 788: p. 422-428.
- 566 31. Manyasree, D., K. Peddi, and R. Ravikumar, CuO nanoparticles: synthesis,
567 characterization and their bactericidal efficacy. *Int J Appl Pharmaceut*, 2017. 9(6): p.
568 71-74.
- 569 32. Jamil, S., M.R.S.A. Janjua, and S.R. Khan, Synthesis and structural investigation of
570 polyhedron Co₃O₄ nanoparticles: Catalytic application and as fuel additive. *Materials*
571 *Chemistry and Physics*, 2018. 216: p. 82-92.
- 572 33. Jamil, S., et al., The first morphologically controlled synthesis of a nanocomposite of
573 graphene oxide with cobalt tin oxide nanoparticles. *RSC advances*, 2018. 8(64): p.
574 36647-36661.
- 575 34. Zaheer, Z., A.-A. Aisha, and E.S. Aazam, Adsorption of methyl red on biogenic Ag@
576 Fe nanocomposite adsorbent: Isotherms, kinetics and mechanisms. *Journal of*
577 *Molecular Liquids*, 2019. 283: p. 287-298.

- 578 35. Sree, G.S., et al., Enhanced UV-Visible triggered photocatalytic degradation of
579 Brilliant green by Reduced Graphene Oxide based NiO and CuO ternary
580 nanocomposite and their antimicrobial activity. *Arabian Journal of Chemistry*, 2020.
- 581 36. Rangel, W.M., R.A.A.B. Santa, and H.G. Riella, A facile method for synthesis of
582 nanostructured copper (II) oxide by coprecipitation. *Journal of Materials Research and*
583 *Technology*, 2019.
- 584 37. Rao, M.P., et al., Photocatalytic properties of hierarchical CuO nanosheets synthesized
585 by a solution phase method. *Journal of Environmental Sciences*, 2018. 69: p. 115-124.
- 586 38. Li, B., et al., A facile one-pot synthesis of Cu₂O/RGO nanocomposite for removal of
587 organic pollutant. *Journal of Physics and Chemistry of Solids*, 2013. 74(4): p. 635-640.
- 588 39. Huo, X., et al., Study on Flash-Point Measurement and Reduced Prediction Model for
589 Ternary Extraction System. *Process Safety and Environmental Protection*, 2020.
- 590 40. Zubair, N.F., et al., A comprehensive thermodynamic and kinetic study of synthesized
591 rGO-ZrO₂ composite as a photocatalyst and its use as fuel additive. *Journal of*
592 *Molecular Structure*, 2019. 1198: p. 126869.
- 593 41. Khan, S.R., et al., Template free synthesis of calcium-tin (CaSn₃) bimetallic micro
594 cubes: Characterization, catalytic activity, adsorption and additive properties. *Chemical*
595 *Physics Letters*, 2020. 739: p. 136917.
- 596 42. Kalaimurugan, K., et al., Combustion analysis of CuO₂ nanoparticles addition with
597 neochloris oleoabundans algae biodiesel on CI engine. *Materials Today: Proceedings*,
598 2020.
- 599 43. Wang, Y. and H. Tian, Study on the construction of YMnO₃/CeO₂ composite
600 photocatalyst heterostructure and photocatalytic degradation of methyl red. *Optik*,
601 2020. 201: p. 163524.
- 602 44. Patil, S., et al., Sulfated TiO₂/WO₃ nanocomposite: An efficient photocatalyst for
603 degradation of Congo red and methyl red dyes under visible light irradiation. *Materials*
604 *Chemistry and Physics*, 2019. 225: p. 247-255.
- 605
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Table 1. Effect of GO-CuO on physicochemical fuel properties.

Parameters	Concentration of catalyst dosage						References
	0 ppm	20 ppm	40 ppm	60 ppm	80 ppm	100 ppm	
Flashpoint (°C)	78	70	66	59	50	-	This work
	71	64	60	-	-	-	[40]
Fire point (°C)	80	75	69	62	58	-	This work
	74	69	54	-	-	-	[40]
Cloud point (°C)	-4	-5	-5	-6	-8	-	This work
	7	5	2	-	-	-	[40]
Pour point (°C)	-14	-15	-15	-17	-19	-	This work
	-11	-12	-13	-	-	-	[40]
Kinematic Viscosity (mm ² /s)	1.93	1.86	1.85	1.84	1.83	-	This work
	2.68	2.86	3.30	-	-	-	[41]
Specific gravity (g/cm ³)	8.27	8.75	8.91	9.12	9.13	-	This work
	8.50	8.53	8.55	-	-	-	[41]
Calorific values (J/g)	43,542	45,304	45,380	45,524	45,634	-	This work
	43,540	-	-	-	-	45,519	[42]

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Table 2. Lattice parameters from XRD analysis for CuO nanoparticles.

Parameters	Outcomes
Formula	CuO
Space group	C1 2/c1 (15)
Cell parameters (Å)	
a (Å)	4.69
b (Å)	3.43
c (Å)	5.13
α (°)	90
β (°)	99.65
γ (°)	90
Crystal system	monoclinic
Number of atoms	22
Coordinates x, y, z for Cu atom	0.25, 0.23, 0.000
Coordinates x, y, z for O atom	-0.01, 0.42, 0.25
Volume (Å ³)	82.47
Calculated density (g/cm ³)	6.50

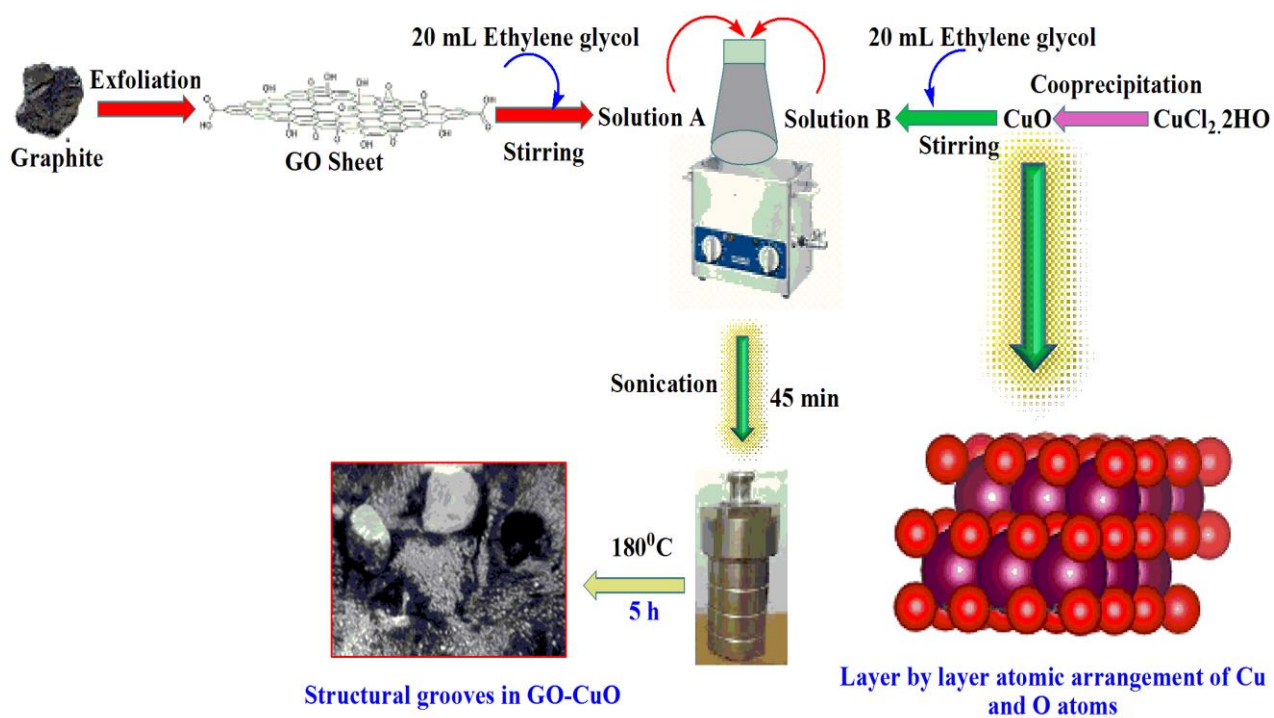
Table 3. Evaluation of kinetic parameters for MR adsorption on CuO, GO and GO-CuO.

Kinetic parameters	MR dye		
	CuO	GO	GO-CuO
Pseudo-first order			
K_1 (1/min)	0.04	0.04	0.03
q_e calculated (mg/g)	0.18	0.16	0.23
q_e experimental (mg/g)	32.14	17.08	34.98
R^2	0.43	0.47	0.95
Pseudo-second order			
K_2 (g/mg min)	0.003	0.001	0.004
q_e calculated (mg/g)	34.84	25	36.36
q_e experimental (mg/g)	32.14	17.08	34.98
R^2	0.98	0.71	0.99
Intra particle diffusion			
R^2	0.94	0.95	0.97

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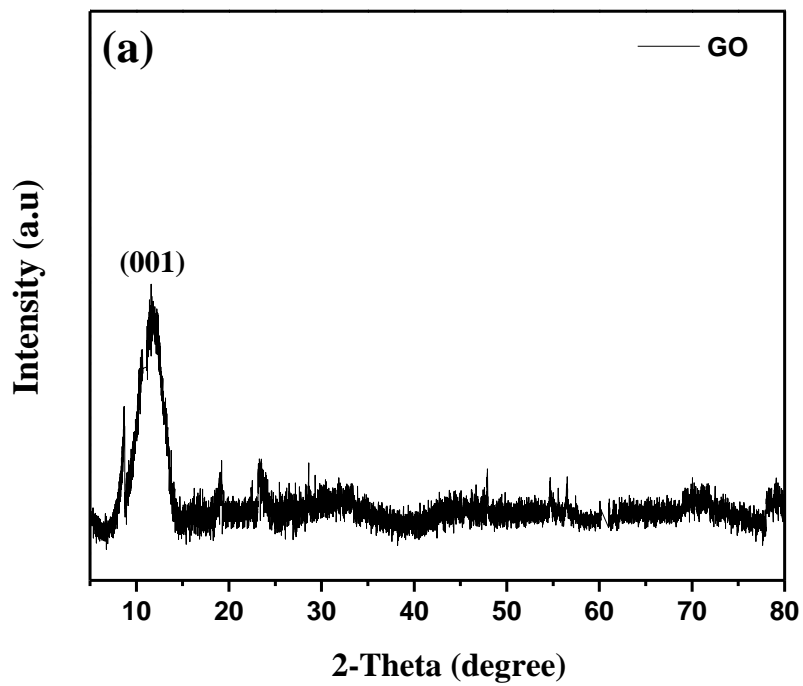


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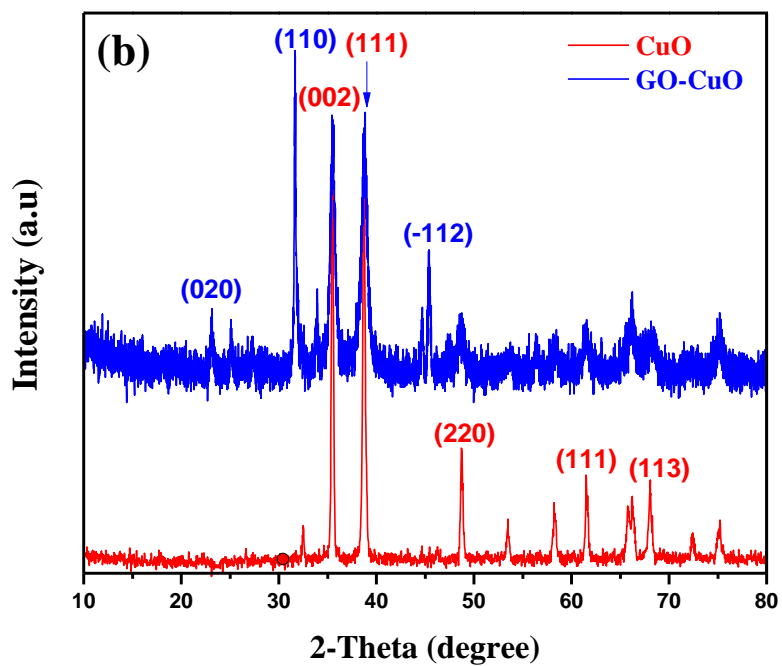
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Fig. 1. Preparation scheme of GO-CuO nanocomposite.

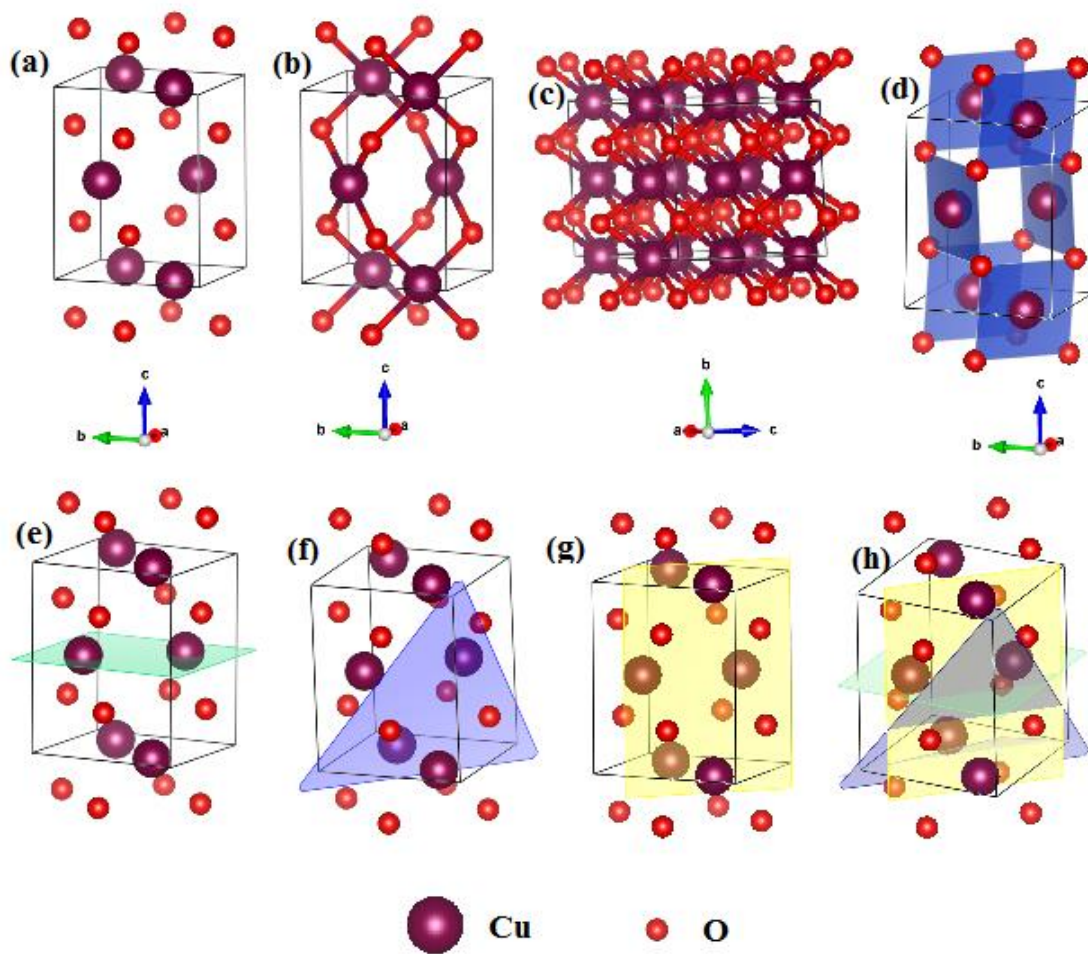


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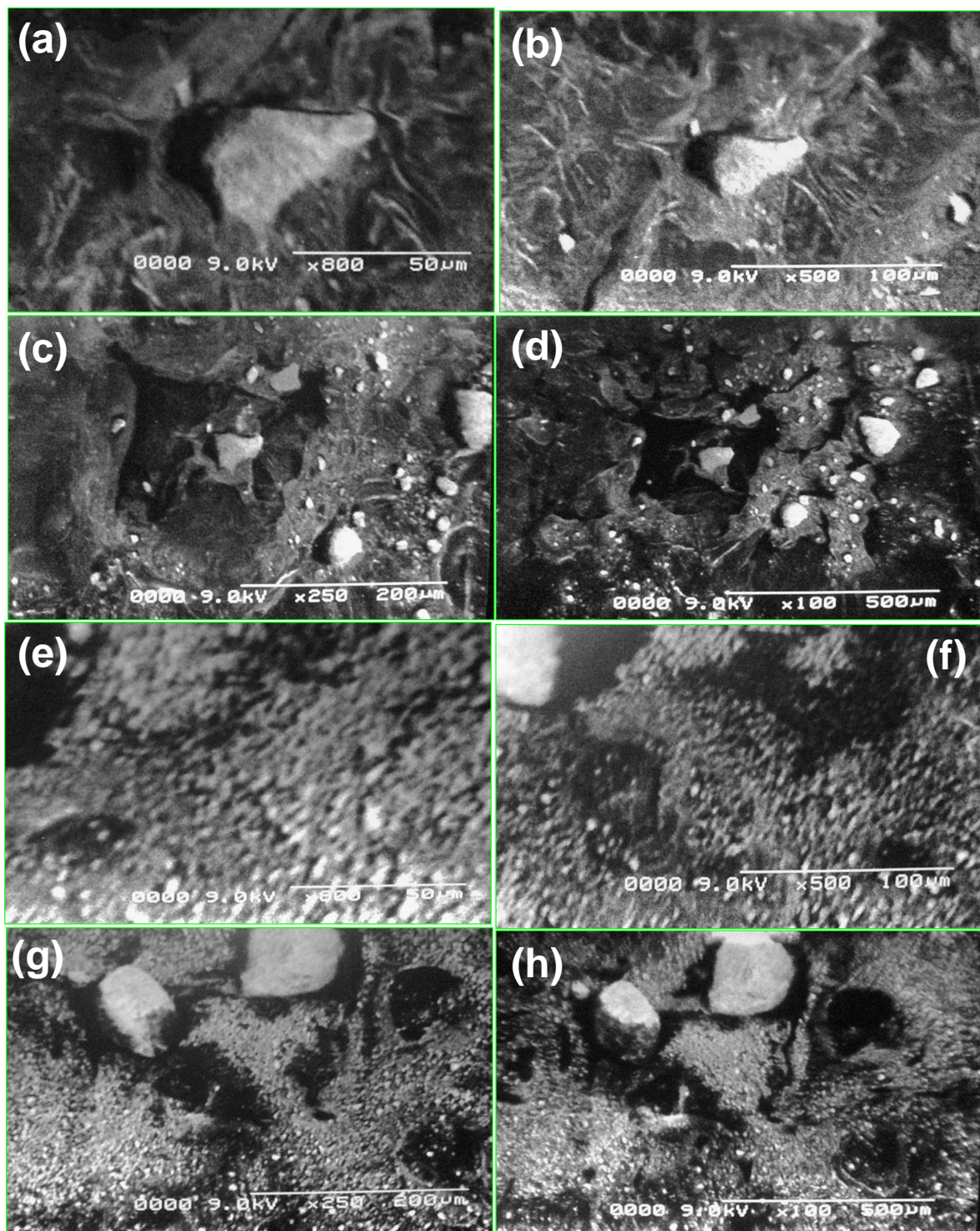
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Fig. 2. X-ray diffraction patterns; (a) graphene oxide, and (b) CuO and GO-CuO.



625

626 **Fig. 3.** Structural model of CuO; (a-b) Position of Cu and O atoms in a monoclinic unit cell, (c) atomic
 627 arrangement with unique b axis, (d) polyhedrons in unit cell, (e) unit cell representation of (002) plane
 628 with d-spacing 2.53°, (f) (111) plane with d-spacing 2.32°, (g) (220) plane with d-spacing 1.87° and (h)
 629 all planes in one unit cell.



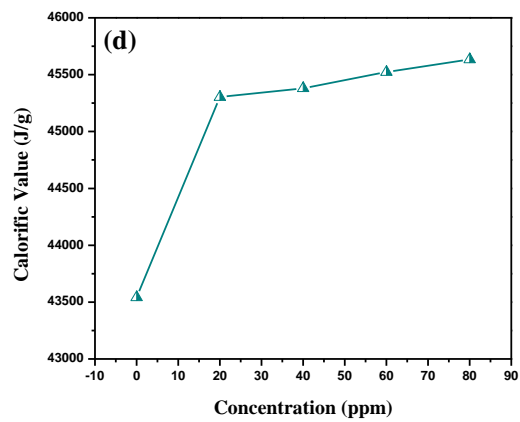
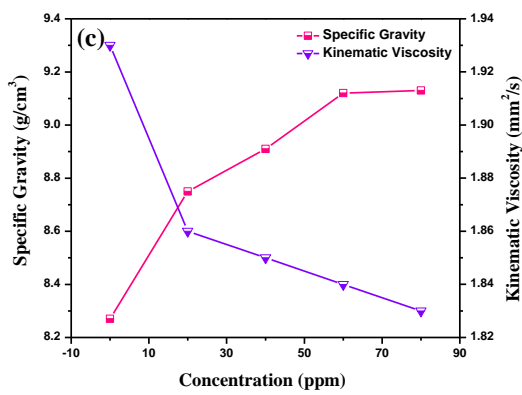
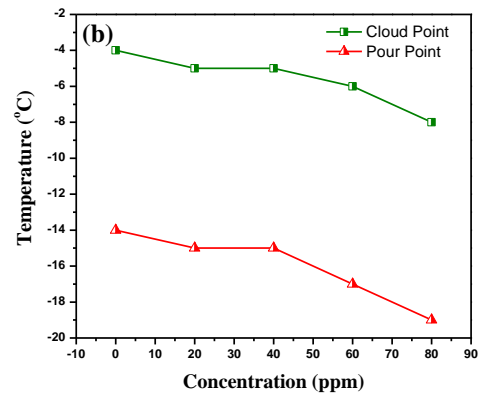
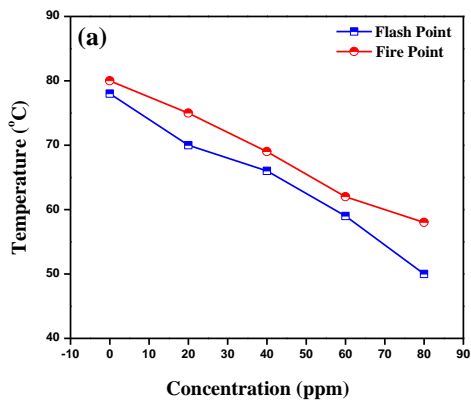
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631 **Fig. 4.** SEM images of CuO nanoparticles; (a) 800× (b) 500× (c) 250× (d) 100× and GO-CuO
632 nanocomposite at (e) 800× (f) 500× (g) 250× (g) 100×.

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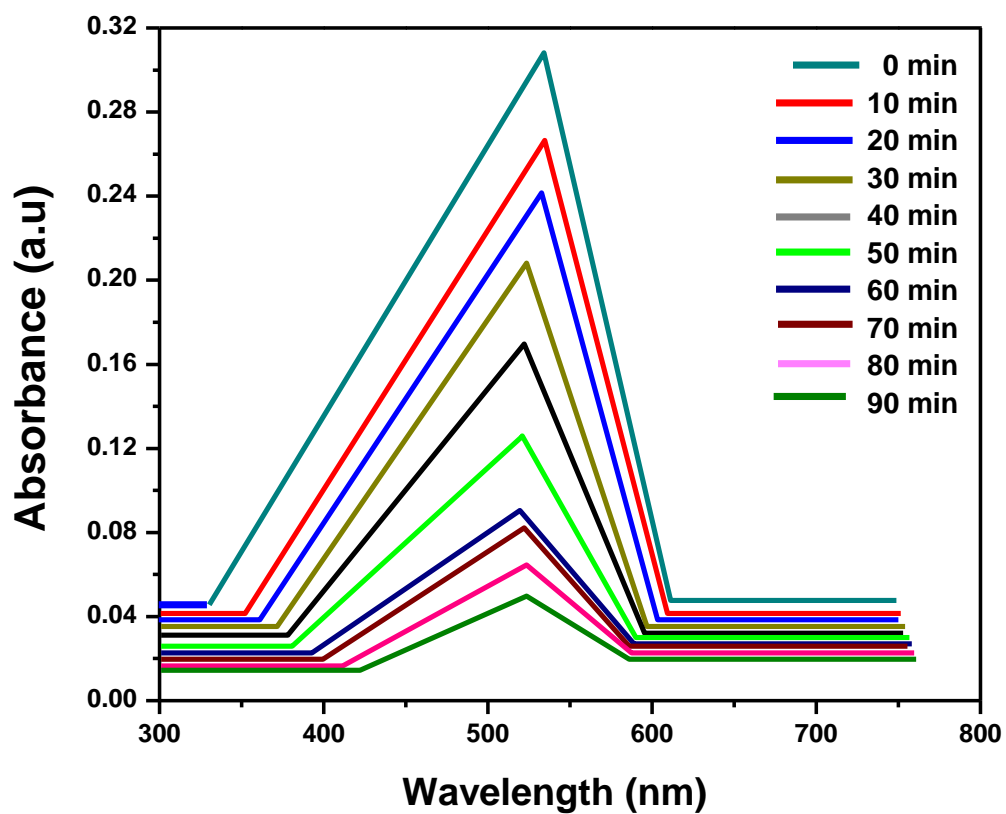
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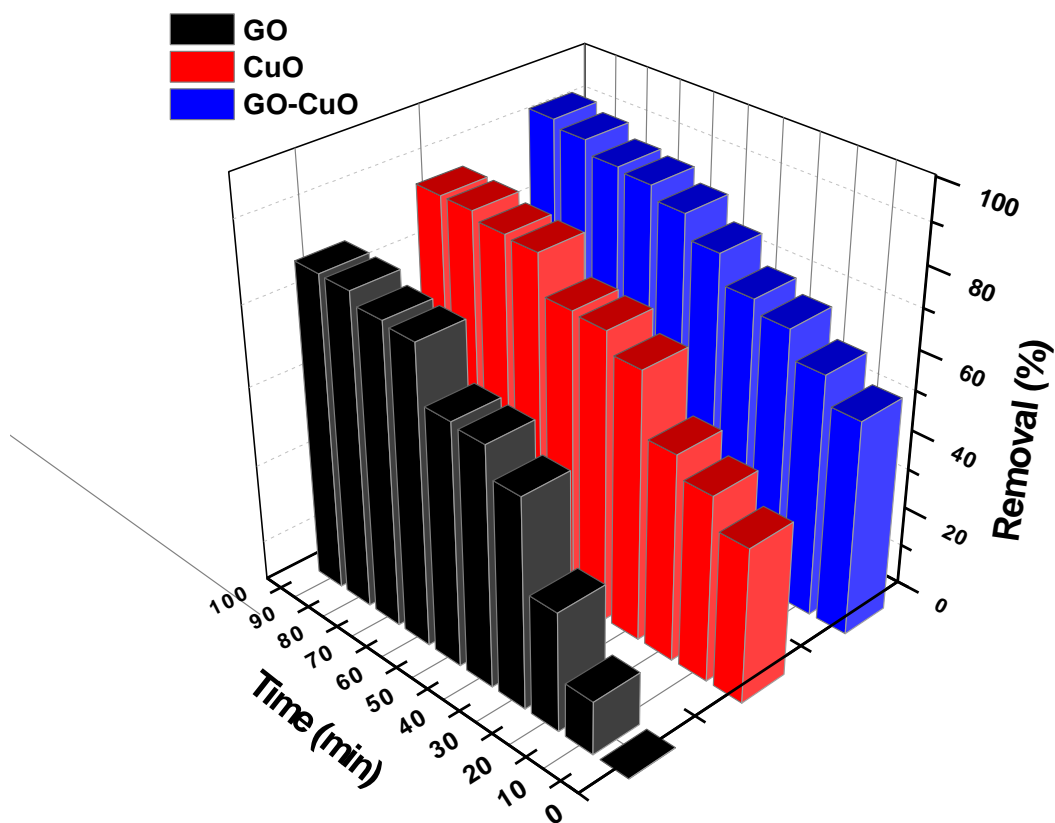
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Fig. 5. Effect of GO-CuO nanocomposite for diesel oil onto; (a) flash point and fire point, (b) cloud point and pour point, (c) specific gravity and kinematic viscosity and (d) calorific value.



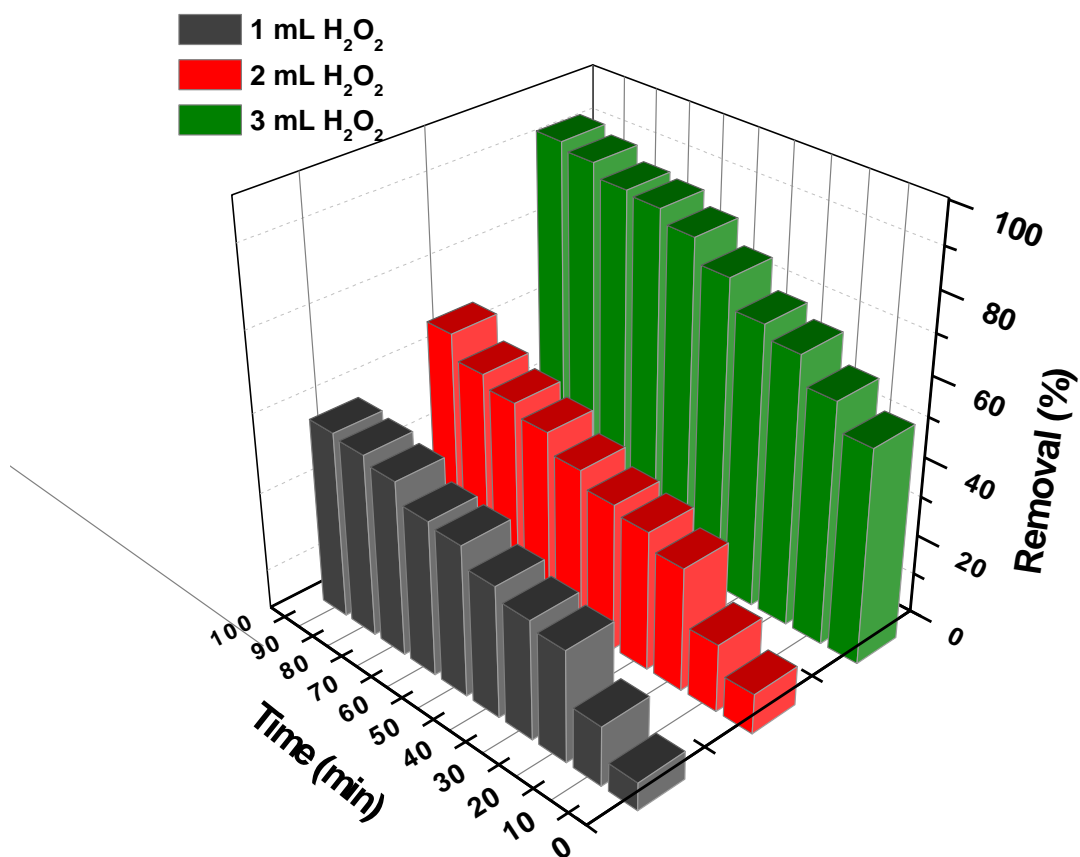
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641 **Fig. 6.** Time dependent UV-visible spectra of catalytic absorbance for MR dye (conditions: [MR
642 dye]=20 ppm, [H₂O₂]= 1.5M, [GO-CuO]=0.35 mg).



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Fig. 7. Effect of GO, CuO and GO-CuO on the percentage removal of MR dye.

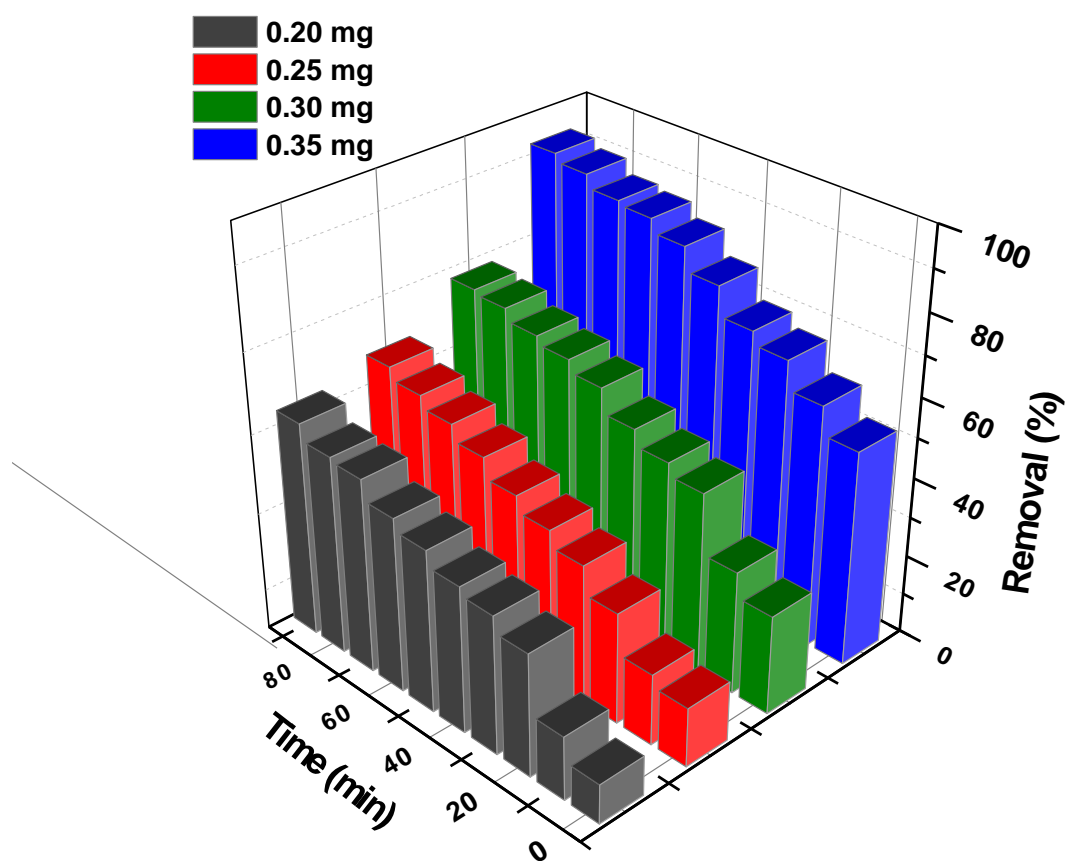


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647 **Fig. 8.** Effect of H₂O₂ concentrations on the percentage removal of MR dye with GO-CuO
 648 nanocomposites.

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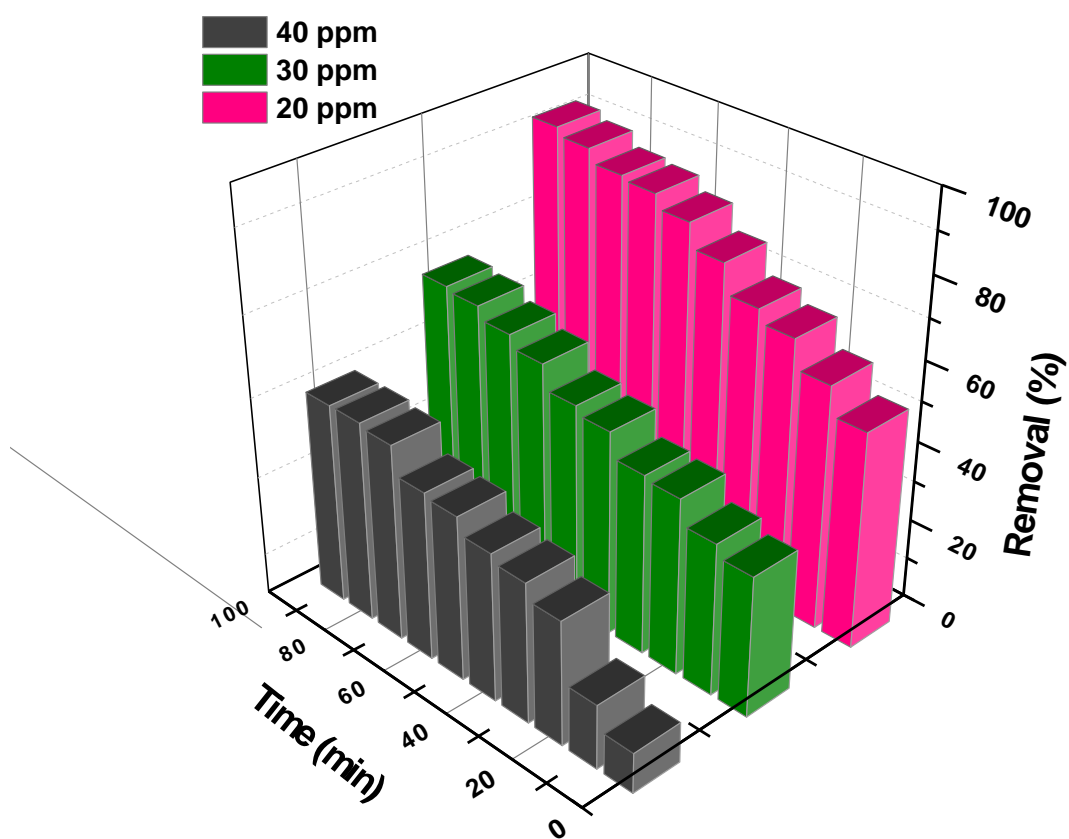
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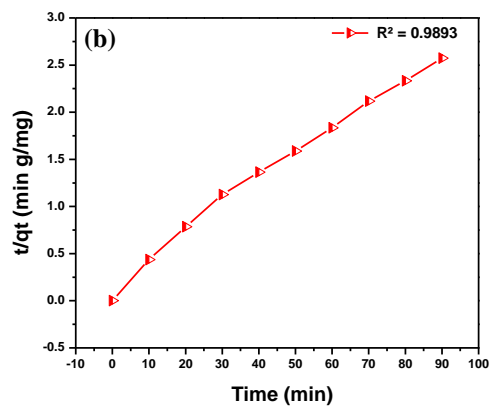
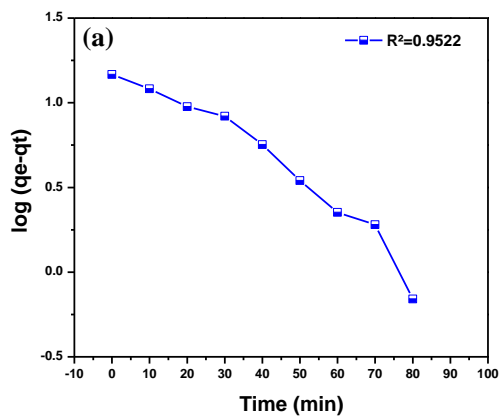
652 **Fig. 9.** Effect of photocatalyst concentrations on the percentage removal of MR dye with GO-CuO
653 nanocomposites.

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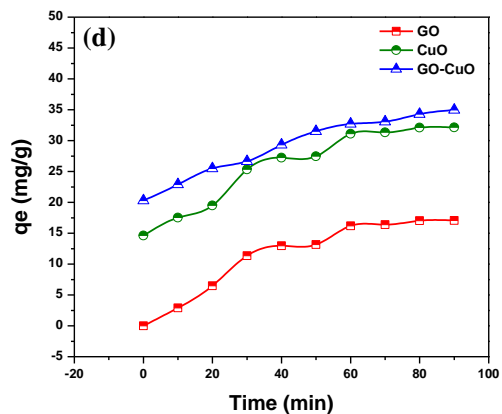
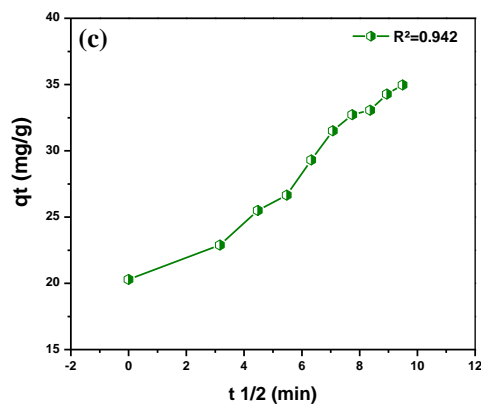


655 **Fig.10.** Effect of initial dye concentrations on the percentage removal of MR dye with GO-CuO
 656 nanocomposites.
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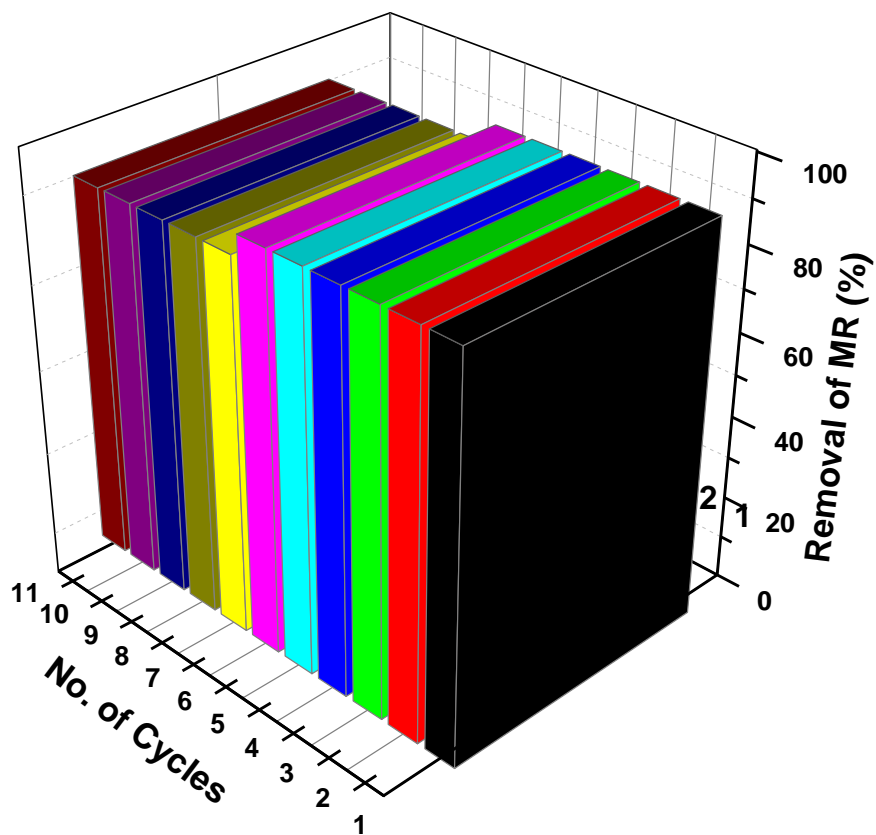


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663 **Fig. 11.** Kinetic models of adsorption under optimized conditions (pH=8.0, [MR]=20 ppm,
664 Catalyst=0.35 mg, agitation time 0–90 min and temperature = 35 °C) for; (a) pseudo-first-order model
665 (b) pseudo-second-order (c) intraparticle diffusion model onto GO-CuO and (d) sorption capacities of
666 GO, CuO and GO-CuO.
667



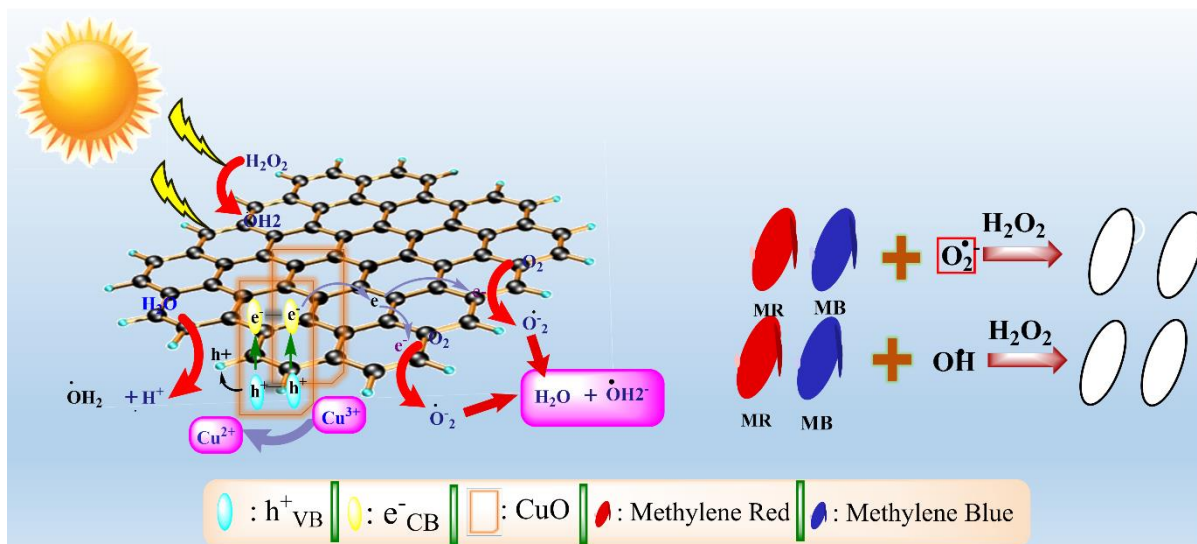
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Fig. 12. Reusability of GO-CuO nanocomposite.

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Graphical Abstract

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