

In-situ electro-generation and activation of hydrogen peroxide using a CuFeNLDH-CNTs modified graphite cathode for degradation of cefazolin

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1 **In-situ electro-generation and activation of hydrogen peroxide using**
2 **a CuFeNLDH-CNTs modified graphite cathode for degradation of**
3 **cefazolin**

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26 **Abstract**

27 The modified multifunctional electrodes for electro-Fenton (EF) process are suggested to
28 be promising cathodes for in situ electro-generation and activation of H₂O₂ to produce hydroxyl
29 radicals ([•]OH). However, heterogeneous EF process still faces the challenges of limited
30 catalytic activity and releasing of massive amounts of transition metals to the solution after
31 removal of organic pollutants. The main aim of the present investigation was to prepare a
32 cathode containing carbon nanotubes (CNTs) and CuFe nano-layered double hydroxide
33 (NLDH) for degradation and mineralization of cefazolin antibiotic through electro-Fenton
34 process. Structural and electrochemical analyses demonstrated that CuFeNLDH-CNTs
35 nanocomposite was successfully incorporated on the surface of graphite cathode. Due to the
36 increased formation of [•]OH in the reactor, the incorporation of CNTs into NLDH matrix with
37 a catalyst loading of 0.1 g substantially improved the degradation efficiency of cefazolin
38 (89.9%) in comparison with CNTs-coated (28.7%) and bare graphite cathode (22.8%) within
39 100 min. In the presence of 15 mM of ethanol, the degradation efficiency of cefazolin was
40 remarkably decreased to 43.7% by the process, indicating the major role of [•]OH in the
41 destruction of target molecules. Acidic conditions favored the degradation efficiency of
42 cefazolin by the modified EF process. Mineralization efficiency of the bio-refractory
43 compound was obtained to be 70.1% in terms of chemical oxygen demand (COD) analysis
44 after 300 min. The gas chromatography-mass spectroscopy (GC-MS) analysis was also
45 implemented to identify the intermediate byproducts generated during the degradation of
46 cefazolin in the CuFeNLDH-CNTs/EF reactor.

47

48 **Keywords:** Electrochemical advanced oxidation processes (EAOPs); Antibiotic compound;
49 Layered double hydroxide; Carbon nanotubes; Fenton reaction.

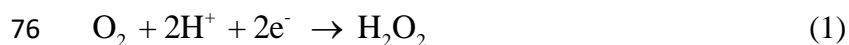
50 **1. Introduction**

51 In recent years, the discharge of wastewaters containing pharmaceutical compounds into
52 aquatic ecosystems has become a great environmental and health concern [1, 2]. Among
53 various groups of pharmaceuticals, antibiotic compounds have been further considered because
54 of their wide implementation for the treatment of bacterial-causing infections [3, 4]. A typical
55 antibiotic model is cefazolin, which is a part of β -lactam cephalosporines antibiotics derived
56 from the *Cephalosporium* fungus. It is a semi-synthetic compound manufactured for the
57 treatment of acute infections in bones, stomach, heart valves and lungs [5, 6].

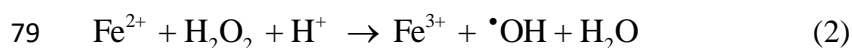
58 Noticeably, even trace amounts of β -lactam antibiotics such as cefazolin in water resources
59 and wastewater treatment plants effluents may lead to adverse effect on aquatic life and
60 subsequently human life [7, 8]. In addition, the presence of antibiotics such as cefazolin in the
61 ecosystem will lead to the development of antibiotic-resistant microbial strains [9]. Microbial
62 resistance against antibiotic drugs has become a major global health concern [10]. Since most
63 antibiotics are categorized as recalcitrant compounds, biological treatment processes are not
64 able to efficiently degrade this type of contaminants [11].

65 Application of efficient chemical treatment processes, especially advanced oxidation
66 processes (AOPs) has been considered for effective destruction and mineralization of these bio-
67 refractory compounds [12-14]. The implementation of AOPs results in the formation of
68 hydroxyl radical ($\cdot\text{OH}$) with high oxidation potential to non-selectively degrade various organic
69 and inorganic substances [15]. Many AOPs have been examined for treating antibiotic
70 compounds. Among them, due to their high effectiveness and low operational (annual) costs,
71 Fenton-based treatment processes and in particular, Fenton's reaction-based electrochemical
72 advanced oxidation processes (EAOPs) have been successfully utilized for the
73 decontamination of antibiotic-polluted water streams [11, 16]. The efficiency of the electro-

74 Fenton (EF) process is significantly affected by the capability of the process to in situ generate
75 H₂O₂ through the cathodic reduction as shown in the following reaction [11]:



77 In the following, the as-generated H₂O₂ molecules react with iron ions as Fenton catalyst to
78 produce •OH in the bulk solution [17]:



80 According to the previous studies, efficient generation of H₂O₂ in EF process can be
81 attained by the immobilization of carbonaceous nanostructures such as carbon nanotubes
82 (CNTs) on the graphite cathode surface [18, 19]. CNTs can offer important benefits for the
83 two-electron reduction of oxygen owing to their good surface activity, high electrical
84 conductivity, and mechanical strength [19]. On the other hand, as an innovative method, the
85 catalyst is immobilized on the cathode surface to continuously generate •OH in the bulk
86 solution. Based on this approach, the stability of the EF process in repeated runs will be
87 increased as well as its cost-effectiveness. Iron ions are constantly regenerated on the surface
88 of the catalyst-coated cathode.

89 Layered double hydroxides (LDHs) are one of the most useful classes of inorganic layered
90 compounds which can be used to host heterogeneous Fenton catalysts on the surface of cathode,
91 improving its structure for the in-situ generation of H₂O₂ and subsequently, the formation of
92 •OH during the EF process. Due to their versatility as well as their unique structure with high
93 porosity and thermal stability, LDHs and their modifications have been extensively utilized as
94 heterogeneous catalysts for numerous applications [20, 21].

95 In this study, Fe together with Cu ions was incorporated into LDH matrix as Fenton
96 reaction's catalysts to avoid the leachate of toxic Fe and Cu ions into the ecosystem.
97 Considering the advantages of nano-materials, the nano-LDH (NLDH) containing Fe and Cu

98 nanostructures was used as an active site to catalyze the generation of free oxidizing agents for
99 the decomposition of target contaminants. CNTs were added to the CuFeNLDH-coated cathode
100 to produce more oxidizing radicals in the solution for the degradation of cefazolin antibiotic.
101 The as-synthesized cathode was characterized by using scanning electron microscopy (SEM),
102 high resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD),
103 Fourier transform infrared spectroscopy (FT-IR), Energy-dispersive X-ray spectroscopy
104 (EDX) equipped with elemental mapping, X-ray photoelectron spectroscopy (XPS), cyclic
105 voltammetry (CV), and linear scan voltammetry (LSV) analyses. Hitherto, no study has been
106 performed and reported regarding the application of CuFeNLDH/CNTs-coated graphite as
107 nanocomposite cathode for the EF process to decontaminate polluted water streams. Chemical
108 oxygen demand (COD) and gas chromatography-mass spectrometry (GC-MS) analyses were
109 also performed to determine the mineralization rate and intermediate byproducts during the
110 degradation of cefazolin.

111

112 **2. Materials and methods**

113 **2.1. Chemicals**

114 Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$: 90%), iron (III) nitrate hexahydrate
115 ($\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$: 99%), ammonium fluoride (NH_4F : 95%), hydrochloric acid (HCl : 37%),
116 sodium sulfate (Na_2SO_4 : 98.5%), hydrogen peroxide (H_2O_2 : 35%), sodium carbonate (Na_2CO_3 :
117 98%), nitric acid (HNO_3 : 65%), sulfuric acid (H_2SO_4 : 98%), ethanol ($\text{C}_2\text{H}_5\text{OH}$: 96%), urea
118 ($\text{CH}_4\text{N}_2\text{O}$: 99.5%), 1,4-benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$: 99%), n-butanol ($\text{C}_4\text{H}_{10}\text{O}$ > 99.7%) and
119 sodium hydroxide (NaOH : 99%) were obtained from Merck (Germany). Pristine multi-walled
120 carbon nanotubes (MWCNTs) with 3-5 nm inner diameter and 8-15 nm outer diameter were
121 obtained from Cheap Tubes (USA). 60% polytetrafluoroethylene (PTFE) solution (Teflon

122 Dispersion, DISP 30) was purchased from DuPont (USA). Graphite plates were purchased
123 from Tabriz Zoghal Co. (Iran). Cefazolin was obtained from Loghman Co. (Iran). The
124 characteristics and chemical structure of cefazolin are presented in Table 1.

125

126 **2.2. Modification of CNTs**

127 For the addition of hydroxyl and carboxyl groups onto the surface of CNTs, a mixture of
128 pristine CNTs and 1: 3 volume ratio of nitric acid and sulfuric acid were sonicated at $80.0 \pm$
129 0.5 °C for 1 h. After washing with deionized water and centrifugation with 3500 ± 50 rpm for
130 30 min, the acid-treated CNTs were dried at 60.0 ± 0.5 °C for 12 h (Fig. S1).

131

132 **2.3. Synthesis of CuFeNLDH-CNTs**

133 The CuFeNLDH-CNTs nanocomposite was synthesized by the hydrothermal method.
134 Appropriate amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (250.0 mmol/L), $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (125.0 mmol/L),
135 NH_4F (312.5 mmol/L), Urea (1250.0 mol/L) and modified CNTs (0.5 g) were mixed in 70 mL
136 deionized water. The resulting solution was stirred with a magnetic stirrer for 30 min. After
137 that, the obtained solution was transferred into a 100 mL Teflon-lined stainless steel autoclave.
138 The sealed autoclave was placed in an oven and kept at 90.0 ± 0.5 °C for 24 h. Finally, as-
139 synthesized CuFeNLDH-CNTs crystals were dried at 50.0 ± 0.5 °C after five times washing
140 (Fig. S2).

141

142 **2.4. Immobilization of CuFeNLDH-CNTs on the graphite plate**

143 In order to clean the surface of the graphite plate, it was immersed in a solution of 10%
144 nitric acid and sonicated using a probe sonicator (Hielscher, UP400S, 400 W, 24 kHz) for 30
145 min. Firstly, 1.4 g PTFE and 0.1 g CuFeNLDH-CNT were added to the mixture of water (30

146 mL) and n-butanol (6% w/w). The obtained suspension was sonicated for 30 min to obtain a
147 highly dispersed mixture. The resulting mixture was heated at 80.0 ± 0.5 °C until an ointment
148 appeared. The resulting ointment was immobilized on the graphite plate and was calcined at
149 350 ± 5 °C for 15 min under nitrogen gas. PTFE in the cathode has two roles: pasting the high
150 surface CuFeNLDH-CNTs into a cohesive layer and imparting some hydrophobic character to
151 the layer. Schematic diagram for the stabilization of nanocomposite on the graphite plate is
152 shown in Fig. S3.

153

154 **2.5. Characterization**

155 XRD analysis (PANalytical X'Pert PRO, Germany) with Cu K α radiation ($\lambda = 0.15406$ nm)
156 was used to determine the crystallite structure of the treated graphite plate at 40 mA and 45 kV.
157 The functional groups of CuFeNLDH, CNTs and CuFeNLDH-CNTs were analyzed by FT-IR
158 spectrometer (Tensor 27, Bruker, Germany), with the KBr pellet in the range of 400–4000 cm⁻¹.
159 ¹. The surface morphology, magnitudes and chemical composition of CuFeNLDH, CNTs,
160 CuFeNLDH-CNTs and the treated graphite electrode were examined by SEM equipped with
161 EDX spectroscopy (Mira3 FEG-SEM Tescan, Czech Republic). HR-TEM images were taken
162 by a high resolution microscope (Hitachi HT-7700, Japan) operating at 120 kV. CV (scan rate
163 of 50 mV/s) and LSV were performed using an electrochemical system (PG-Stat 30,
164 Netherlands). XPS spectra were also recorded using Kratos AXIS UltraDLD spectrometer
165 (UK).

166

167

168 **2.6. Apparatus and analyses**

169 For EF experiments, the anode was a platinum sheet (6.25 cm²) and the cathode was the
170 CuFeNLDH-CNTs-coated graphite plate (3 cm²). The distance between the platinum sheet and

171 the treated graphite plate was 1 cm. EF experiments were done at room temperature (25.0 ± 0.5
172 °C) using an undivided cylindrical glass reactor containing 80 mL cefazolin-contained solution
173 as the target pollutant and Na_2SO_4 as the supporting electrolyte with certain concentrations.
174 Both electrodes were connected to a DC power supply (Adak PS-808, Iran). During the reaction
175 time, an air pump (RS-510, China) was used for air injection into the reactor. Ozone gas (ozone
176 generator, BE-72, Iran) was bubbled into the bulk solution by means of a porous diffuser. It
177 was coupled with an oxygen concentrator (Airsep, USA). The cefazolin degradation was
178 measured by determining the absorbance at a wavelength of 260 nm with a UV-Vis
179 spectrophotometer (SU-6100, Philler scientific, USA). The concentration of H_2O_2 electro-
180 generated on the surface of bare graphite electrode and modified electrodes were determined
181 by the iodide method [22]. The COD concentration before the treatment process and the
182 residual COD after the treatment process were determined by a standard method (method no.
183 5220) [23], using Palin test (United Kingdom) apparatus. The intermediates produced during
184 the cefazolin degradation were determined by Agilent 6890 gas chromatography-mass
185 spectrometry (GC-MS) and an Agilent 5973 mass spectrometer (Canada).

186

187 **3. Results and discussion**

188 **3.1. Characterization**

189 **3.1.1. SEM images**

190 Fig. 1 exhibits the SEM images of CuFeNLDH (a-d), pristine CNTs (e-h), CuFeNLDH-
191 CNTs nanocomposite (i-l) and CuFeNLDH-CNTs-coated graphite cathode (m-p). As can be
192 seen in Fig. 1 (a-d), CuFeNLDH consists of microspheres decorated with nano-sheets with an
193 average diameter of 26 nm. The SEM images of CuFeNLDH-CNTs nanocomposite display
194 that CNTs are successfully incorporated into CuFeNLDH nano-sheets (Fig. 1 (i-l)).
195 CuFeNLDH-CNTs nanocomposite coated on graphite plate can be also observed in Fig. 1 (m-

196 p). The presence of nano-tubes in the structure of CuFeNLDH-CNTs nanocomposite
197 immobilized on the surface of graphite cathode can be clearly seen in Fig. 1 (o and p).

198

199 **3.1.2. EDX spectra**

200 EDX spectroscopy equipped with SEM analysis was implemented to specify elemental
201 composition of CuFeNLDH, CNTs, CuFeNLDH-CNTs and CuFeNLDH-CNTs-coated
202 graphite cathode (Fig. S4 (a-d)). The results revealed that the CuFeNLDH contained O, N, C,
203 Cu and Fe elements (Fig. S4 (a)). According to Fig. S4 (b), the CNTs is composed of C and O
204 elements. Compared with non-immobilized CuFeNLDH-CNTs, the amount of C element in
205 the structure of the modified cathode remarkably increased due to the immobilization of
206 CuFeNLDH-CNTs on the surface of graphite cathode. The elemental mapping images of
207 CuFeNLDH/CNTs-coated graphite cathode was also performed (Fig. S5). As shown, the
208 elements in the composition of the modified cathode are uniformly distributed, indicating the
209 suitable structure of as-synthesized cathode for the reduction of oxygen molecule and
210 generation of $\cdot\text{OH}$ via the whole surface of cathode through the interaction of Cu and Fe ions
211 with electro-generated H_2O_2 .

212

213 **3.1.3. HR-TEM images**

214 HR-TEM images of CuFeNLDH and CuFeNLDH-CNTs are exhibited in Fig. 2. Fig. 2 (a
215 and b) indicates the formation of sheet-like CuFeNLDH nanostructures with regular size and
216 relatively uniform size distribution. The size of thickness and width of CuFeNLDH
217 nanostructures are in the range of 10.00-30.00 and 20.00-50.00 nm, respectively (Fig. 2 (e and
218 f)). The images of CNTs-implanted CuFeNLDH show the presence of ultrafine structures in
219 the composition of nanocomposite (Fig. 2 (c and d)), creating high surface area and more
220 reaction sites for the generation of H_2O_2 molecules and $\cdot\text{OH}$ radicals to catalytically convert

221 the target antibiotic pollutant. Fig. 2 (d) displays that CNTs are successfully introduced into
222 the CuFeNLDH nano-sheets.

223

224 **3.1.4. XRD patterns**

225 The XRD patterns of CuFeNLDH, CuFeNLDH-CNTs, and CuFeNLDH-CNTs-coated
226 graphite are shown in Fig. 3 (a-c). For the XRD pattern of CuFeNLDH (Fig. 3a), characteristic
227 peaks placed at 12.8, 25.8, 33.6, 36.5 and 43.2° correspond to the (003), (006), (012), (015)
228 and (018) crystal plane according to JCPDS card no. 41-1428 [24]. In the case of XRD patterns
229 obtained for CuFeNLDH-CNTs (Fig.3b) and CuFeNLDH-CNTs-coated graphite (Fig.3c), the
230 diffraction peak located at about 26.5° is associated with the (002) reflection of the CNTs and
231 graphite based on JCPDS card no. 74-444 [25].

232

233 **3.1.5. FT-IR spectra**

234 The FT-IR spectra of CuFeNLDH, CNTs and CuFeNLDH-CNTs samples are displayed in
235 Fig. S6. FT-IR spectrum of CuFeNLDH exhibits the peaks at 464 and 582 cm⁻¹ attributed to
236 the Fe-O vibration [26]. The peak placed at 518 cm⁻¹ indicates the Cu-O bond [27]. A broad
237 and intense peak was observed at 3452 cm⁻¹, related to the O-H stretching vibration [28, 29].
238 The weak peaks located at 2854 to 2925 cm⁻¹ are ascribed to symmetric and asymmetric
239 stretching of C-H bond, respectively [30]. Moreover, the peaks at 1386, 1687 and 875 cm⁻¹ can
240 be related to C-N, C=O and C-O vibrations, respectively [31, 32]. The peaks for C=O vibration
241 (1645 cm⁻¹) and C-N vibration (1126 cm⁻¹) can be observed in the spectrum of the modified
242 CNTs [33]. As mentioned, the peak at 3458 cm⁻¹ represents the O-H group in the structure of
243 CuFeNLDH-CNTs [34]. However, CuFeNLDH-CNTs spectrum shows an absorption band at
244 516 cm⁻¹ attributed to Cu-O vibrations [26] and a peak at 680 cm⁻¹ related to Fe-O vibration
245 [35].

246

247 **3.1.6. XPS**

248 XPS analysis was performed for CuFeNLDH, CuFeNLDH/CNTs, and CuFeNLDH-CNTs-
249 coated graphite cathode whose results are presented in Fig. 4. As can be seen in XPS full spectra
250 of the samples (Fig. 4 (a-c)), CuFeNLDH is composed of O (39.53%), Cu (27.37%), Fe
251 (15.71%), C (12.46%) and N (4.93%) elements. CuFeNLDH/CNTs sample contains O, Cu, Fe,
252 C and N elements with 38.42, 18.82, 8.71, 30.13 and 3.92 atomic percent (At%), respectively.
253 The higher At% of carbon in the structure of the modified cathode compared with
254 CuFeNLDH/CNTs sample is owing to the immobilization of CuFeNLDH-CNTs on the surface
255 of graphite cathode. It was found that the Fe/Cu At% ratio in CuFeNLDH, CuFeNLDH/CNTs,
256 and CuFeNLDH-CNTs-coated graphite cathode was 0.57, 0.46 and 0.53 which is in good
257 accordance with 1/2 molar ratio of iron/copper precursors utilized in the preparation of the
258 samples. High-resolution XPS spectra of Fe 2p, Cu 2p and O 1s are shown in Fig. 4 (d-l). Fig.
259 4 (d and e) shows the presence of three peaks at ~712, ~719 and ~725 eV, which are attributed
260 to Fe 2p_{1/2}, Fe 2p_{3/2} and their satellite, demonstrating that the main part of iron in the structure
261 of CuFeNLDH and CuFeNLDH/CNTs samples is in trivalent state [36]. After immobilizing
262 CuFeNLDH/CNTs on the graphite surface, the peak at ~719 eV nearly disappeared and a new
263 peak was observed at ~708 eV corresponding to Fe²⁺ ion (Fig. 4 (d-l)) [37]. This observation
264 demonstrated that a part of Fe³⁺ in the structure of CuFeNLDH was reduced to Fe²⁺ during the
265 calcination of the CuFeNLDH/CNTs-modified electrode at 350 ± 5 °C under nitrogen
266 atmosphere. The Cu 2p XPS spectra of CuFeNLDH and CuFeNLDH/CNTs (Fig. 4 (g and h))
267 exhibit the peaks at ~935, ~942, ~955 and ~962 eV which illustrate copper oxidation state of
268 2+ [38]. Compared with CuFeNLDH and CuFeNLDH-CNTs, the intensities of the peaks
269 observed in high-resolution spectrum of Fe 2p were considerably decreased for CuFeNLDH-
270 CNTs-coated graphite (Fig. 4 (f)) and Cu 2p peaks became indistinguishable from background

271 noise (Fig. 4 (i)). This can be related to the immobilization of CuFeNLDH-CNTs on the
272 graphite plate using PTFE binder which leads to a decrease in Fe and Cu contents and the
273 variation of their surrounding electron density due to the presence of adjacent species [39, 40].
274 As shown in high-resolution XPS spectra of O 1s (Fig. 4 (j-l)), there is a single peak at binding
275 energy of ~ 533 eV which can be ascribed to OH^- belonging to metal hydroxides or hydroxyl
276 groups [41].

277

278 **3.1.7. CV and LSV curves**

279 The electrochemical performance of the bare graphite cathode was compared with graphite
280 cathodes modified with CuFeNLDH/CNTs nanocomposite using cyclic voltammetry (CV)
281 analysis. Fig. 5 (a) and (b) show the results of CV analysis carried out in the potential range of
282 -0.7 - 1.0 V with a scan rate of 50.0 mV/s in N_2 - and O_2 -saturated solutions, respectively. A
283 reduction peak was detected at the potential around -0.1 V in oxygen saturated solution.
284 However, no obvious reduction peak was observed for N_2 saturated solution, and its reductive
285 current was slightly lower than that of in O_2 -saturated solution, revealing that the prepared
286 cathodes had high activity toward oxygen reduction. On the other hand, the graphite cathodes
287 modified with CuFeNLDH/CNTs nanocomposite have a higher oxygen evolution potential
288 than that of the bare graphite cathode. Linear scan voltammetry (LSV) analysis was also used
289 to further evaluate the electrochemical properties of the modified graphite cathodes in
290 comparison with the bare cathode (Fig. 5 (c)). Accordingly, the results of LSV analysis verified
291 the results of CV analysis. The high oxygen evolution potential of the cathodes leads to the
292 increased generation of hydrogen peroxide and subsequently, increased $\cdot\text{OH}$ in the bulk
293 solution. Moreover, high oxygen evolution potential reduces power loss during the
294 electrochemical-based treatment process, leading to the enhanced cost-effectiveness of the
295 process and its current efficiency [42]. At a specified potential, lower increase in the current of

graphite cathodes modified with CuFeNLDH/CNTs nanocomposite was obtained in comparison with that of the bare cathode. The electroactive surface area of the electrodes were determined in the ferrocyanide system ($[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$) based on the Randles-Sevcik equation (Eq. 3) [43]:

$$I_p = 2.69 \times 10^5 \times AD^{1/2}n^{3/2}\gamma^{1/2}C \quad (3)$$

where I_p is the peak current (A), A is the geometric area of the electrode (cm^2), D is the diffusion coefficient of the probe molecule ($7.60 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), C is the concentration of $[\text{Fe}(\text{CN})_6]^{4-}$ in solution ($1 \times 10^{-5} \text{ mol/cm}^3$), $n = 1$ is the number of electrons involved in the redox $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ reaction and γ is the scan rate (0.05 V s^{-1}). As displayed in Fig. 5 (b), the peak currents of both graphite/CNTs (0.1 g) and graphite/NLDH-CNTs (0.1 g), were higher than that of bare graphite cathode. Accordingly, electroactive surface area was calculated as 5.61, 8.82 and 8.29 for the bare graphite, graphite/CNTs (0.1 g) and graphite/NLDH-CNTs (0.1 g), respectively. The electroactive surface area is one of the important characteristics of the cathode that can potentially enhance the efficiency of the EF process in terms of hydrogen peroxide generation.

311

3.2. Comparison of the performance of different electrodes

A comparative study was performed before the evaluation of the effect of the main operational parameters on the efficiency of the treatment process. The results of these preliminary experiments are provided in Fig. 6 (a). Based on the data obtained, the immobilization of CNTs on the surface of the bare cathode resulted in an insignificant increase in the degradation efficiency of cefazolin compared with the bare cathode (increasing from 22.8% to 28.7%). Interestingly, an obvious increase in the degradation of cefazolin occurred when the CNTs were incorporated into CuFeNLDH lattice. Due to the facile interchangeability of implanted anions and uniform distribution of metal cations in the brucite-like layers of the

321 compound, LDHs exhibit catalytic activity as semiconductor with high stability to be used in
322 various systems including catalytic treatment processes [44]. Particularly, Fe together with Cu
323 ions which are incorporated into LDH matrix act as Fenton reaction's catalysts [20]; thus, the
324 presence of these ions in the structure of LDH leads to the formation of $\cdot\text{OH}$ through the
325 interaction with as-generated H_2O_2 molecules, which resulted in the enhanced degradation
326 efficiency of cefazolin antibiotic by the electro-Fenton process in comparison with the
327 application of CNTs alone. However, an optimum amount of CuFeNLDH-CNTs
328 nanocomposite immobilized on the cathode surface is required to attain the maximum
329 efficiency. The degradation efficiency of cefazolin increased from 48.0% to 69.8% when the
330 amount of CuFeNLDH-CNTs increased from 0.05 to 0.10 g, respectively; while increasing the
331 amount of CuFeNLDH-CNTs up to 0.15 g led to a slight decrease in the degradation efficiency
332 of the pollutant (66.3%). Although the efficiency of CuFeNLDH/CNTs-equipped electro-
333 Fenton process for the degradation of target compound can be enhanced by increasing the
334 amount of coated catalyst; however, increasing the amount of CuFeNLDH/CNTs may cause
335 mass transfer limitation on the cathode surface [45], leading to the reduced formation of
336 oxidizing agents in the electrochemical cell. Moreover, the aggregation of coated catalyst on
337 the surface of the cathode is inevitable at higher amounts which may be the dominating factors
338 leading to the loss of catalyst [46]. Overall, the agglomeration of catalyst or increasing the
339 thickness of the coated catalyst leads to the reduced reactive sites for the reduction of diffused
340 oxygen molecules. Furthermore, protons with small size and high mobility can permeate into
341 the thin film of the catalyst better than the thick layer [47]. Therefore, in the present study, the
342 catalyst loading of 0.10 g was considered as the optimum value in comparison with other values
343 (0.05 and 0.15 g) considering economic and applicability point of view. Fig. 6 (b) shows the
344 concentration of H_2O_2 produced during the EF process on the bare graphite cathode, CNTs-
345 coated graphite and graphite cathodes modified with different amounts of CuFeNLDH/CNTs

346 nanocomposite. Comparatively, the amount of electro-generated H₂O₂ decreased when the
347 cathode surface was coated with CuFeNLDH/CNTs in comparison with the bare and CNTs-
348 coated graphite. This can be due to the interaction of electro-generated H₂O₂ with Fe and Cu
349 ions in the structure of NLDH, thereby producing [•]OH and HO₂[•] radicals in the solution for the
350 efficient degradation of cefazolin according to Eqs. (4-7) [48]:

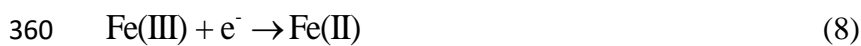


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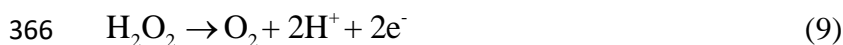


356

357 Based on the above reactions, the presence of CuFeNLDH on the cathode surface inhibits
358 the accumulation of H₂O₂ molecules in the bulk solution. During the EF process, recycling
359 potential of iron species can easily take place through the following equation:



361 As-converted Fe(II) can directly react with hydrogen peroxide to produce [•]OH radicals and
362 concurrently be converted to Fe(III) ions. That is why the major oxidizing agent in the
363 CuFeNLDH-CNTs/EF reactor was still [•]OH radicals. It should not be overlooked that part of
364 hydrogen peroxide molecules may be oxidized on the surface of Pt anode, generating oxygen
365 molecules in the EF reactor [49]:



367

368

369 **3.3. Effect of operational parameters**

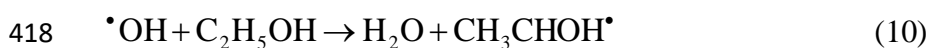
370 The effect of initial pH on the degradation efficiency of cefazolin is displayed in Fig. 7 (a).
371 As shown, the acidic conditions favored the removal of target pollutant by the CuFeNLDH-
372 CNTs/EF process. An increase in the initial pH from 3.0 to 11.0 led to a decrease in removal
373 efficiency from 95.8% to 53.3%, respectively. Actually, the formation of hydrogen peroxide
374 through cathodic reduction is increased under acidic conditions, thereby leading to enhanced
375 production of $\cdot\text{OH}$ in the CuFeNLDH-CNTs/EF reactor. Based on Fig. 7 (a), the change in the
376 degradation efficiency of cefazolin was not significant in the pH range of 3.0-6.0 (decreasing
377 from 95.8% to about 90.0%); thus, the pH value of 6.0 was chosen as the selective pH for
378 conducting the rest of the experiments, while taking cost-efficiency of the treatment system
379 into account. The effect of the applied current on the degradation efficiency of cefazolin by the
380 EF process was assessed (Fig. 7 (b)). Obviously, increasing the applied current in the range of
381 150.0-400.0 mA resulted in the enhanced degradation efficiency of cefazolin from 39.7% to
382 92.8% over the reaction time of 100 min. However, as shown in Fig. 7 (b), increasing the
383 current from 300.0 to 400.0 mA did not significantly influence the efficiency of the EF process
384 (not more than 3.0% increase in the degradation efficiency). In fact, the efficiency of the
385 process operated at these two applied currents was almost the same. Thus, the current intensity
386 of 300.0 mA was considered in the following experimental runs. The application of higher
387 applied currents results in the in-situ generation of more free radicals through the
388 CuFeNLDH/CNTs-coated graphite cathode [50]. Furthermore, increasing the current intensity
389 quickens the diffusion rate of the reactants in the bulk solution, bringing about the improved
390 efficiency of the EF reactor. The results of the effect of cefazolin concentration on its
391 degradation efficiency are presented in Fig. 7 (c). As a result, the degradation efficiency
392 decreased from 45.78% to 95.5% as the initial concentration of cefazolin decreased from 40.0
393 to 10.0 mg/L, respectively. Clearly, higher amounts of oxidizing agents are required to treat
394 the solution containing higher concentrations of cefazolin to attain the pre-determined

395 efficiency [51]. The effect of supporting electrolyte concentration on the degradation efficiency
396 of cefazolin was also examined by varying the sodium sulfate concentration in the range of
397 25.0-100.0 mmol/L. According to Fig. 7 (d), rapid increase in the degradation efficiency of
398 cefazolin from 59.5% to about 90.0% was observed when the supporting electrolyte
399 concentration increased from 25.0 to 50.0 mmol/L; while, increasing its concentration from
400 50.0 to 75.0 mmol/L did not meaningfully influence the efficiency of the EF process over the
401 reaction time of 100 min. Noticeably, increasing the electrolyte concentration from 75.0 to
402 100.0 mmol/L led to a substantial decrease in the degradation efficiency of cefazolin from
403 92.7% to 82.2%, respectively. It can be deduced that the amount of supporting electrolyte
404 should be optimized to operate the treatment process cost-efficiently for full-scale applications.
405 Considering the importance of this issue, the electrolyte concentration of 50.0 mmol/L was
406 chosen for conducting the next experiments.

407

408 **3.4. Effect of scavenging compounds**

409 The effect of some main scavenging compounds on the degradation efficiency of cefazolin
410 by the CuFeNLDH-CNTs/EF process was evaluated to specify not only the efficiency of the
411 process under adverse conditions but also to determine the role of free oxidizing species in the
412 degradation of target contaminants (Fig. 8). In this regard, inorganic (sodium carbonate) and
413 organic (ethanol (EtOH) and benzoquinone (BQ)) scavenging compounds in the concentration
414 range of 5.0-15.0 mmol/L were added to the cefazolin-contained solution to assess the change
415 in the efficiency of the CuFeNLDH-CNTs/EF process. As illustrated in Fig. 8 (a), the presence
416 of ethanol ($\cdot\text{OH}$ scavenger) remarkably reduced the degradation efficiency of cefazolin by the
417 EF process according to the following equation [52]:



419 At ethanol concentrations of 5.0, 10.0 and 15.0 mmol/L, the degradation efficiencies of
420 62.3%, 53.1% and 43.7% were obtained, respectively; while in the absence of ethanol the
421 degradation efficiency of about 90.0% was achieved within 100 min. The presence of BQ ($O_2^{\bullet-}$
422 scavenger) led to the decreased degradation efficiency of cefazolin (Fig. 8 (b)). The scavenging
423 characteristic of BQ is represented through the following equation [53]:



425 BQ is recognized as high potential superoxide anions ($O_2^{\bullet-}$) scavenger [54]. At BQ
426 concentrations of 5.0, 10.0 and 15.0 mmol/L, the degradation efficiencies of 76.0%, 69.7% and
427 59.1% were obtained, respectively. Results of the effect of carbonate ions on the degradation
428 efficiency of cefazolin are displayed in Fig. 8 (c). The decreased degradation efficiency of
429 cefazolin in the presence of carbonate ions is associated with its reaction with $\bullet\text{OH}$ radical to
430 produce carbonate radicals with lower oxidation potential as represented in the equation below
431 [17]:



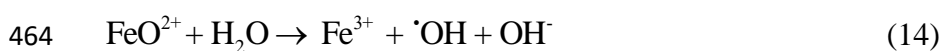
433 The degradation efficiency of cefazolin decreased from 90.0% to 80.3%, 69.7% and 51.5%
434 in the presence of 5.0, 10.0 and 15.0 mmol/L sodium carbonate, respectively. Based on the
435 results obtained, the presence of ethanol led to the most suppressing effect on the degradation
436 of cefazolin through the CuFeNLDH-CNTs/EF process in comparison with both BQ molecules
437 and carbonate ions. Considering $\bullet\text{OH}$ radical scavenging properties of ethanol, indicating the
438 major role of $\bullet\text{OH}$ radical in the degradation of antibiotic molecules through the EF process
439 [55], shows that the result is consistent with those obtained and deduced at the end of
440 preliminary experiments data section.

441

442

443 3.5. Gas injection

444 Fig. 9 shows the effect of air, O₂, O₃, and Ar injected into the solution on the efficiency of
445 the CuFeNLDH-CNTs/EF process. The addition of O₂ and O₃ enhanced the degradation of
446 cefazolin through the EF process, while Ar sparging led to a significant drop in the degradation
447 efficiency of cefazolin compared with the addition of air. Clearly, the injection of pure oxygen
448 into the bulk solution leads to highly efficient electro-generation of hydrogen peroxide and its
449 conversion to [•]OH radical in comparison with ambient air. Furthermore, oxygen molecules
450 dissolved in the solution react with Fe ions, generating superoxide anions [56]. As previously
451 mentioned, the addition of BQ demonstrated the role of this type of free radical, but to a lesser
452 extent than [•]OH radical, in degrading the target pollutant. The highest degradation efficiency
453 was attained when ozone gas was injected into the EF reactor. The interaction of ozone
454 molecules with electro-generated hydrogen peroxide produces [•]OH radicals in the solution.
455 Furthermore, the rest of as-generated hydrogen peroxide is dissolved in the liquid phase and
456 dissociates into hydroperoxide (HO₂⁻) anions, initiating a radical chain reaction to form extra
457 [•]OH radicals thanks to the reaction with ozone gas [57]. Similar results have been reported by
458 Shen et al. in the case of the catalytic decolorization of wastewater through the ozone/Fenton
459 treatment process [58]. From another point of view, when ozone is injected into the
460 CuFeNLDH-CNTs-equipped EF reactor, recycled Fe²⁺ play catalytic role for the conversion of
461 ozone to [•]OH radical. The catalytic reaction of ozone with Fe ions also produces FeO²⁺ species,
462 which gradually changes to [•]OH radical [59]:



465

466 3.6. COD, GC-MS, AAS and stability studies

467 The progress in the mineralization of the target bio-refractory compound was checked
468 via COD analysis over the reaction time of 300 min. Under current intensity of 300.0 mA, the
469 initial COD of the cefazolin-contained solution decreased from 264 mg/L to 79 mg/L by the
470 CuFeNLDH-CNTs/EF process (mineralization efficiency of 70.1%). This result indicated the
471 acceptable destruction and mineralization of the cefazolin antibiotic when it was treated
472 through the CuFeNLDH-CNTs/EF process. The enhanced degradation and mineralization of
473 cefazolin in the EF process equipped with CuFeNLDH-CNTs-coated graphite cathode were
474 mainly the result of the improved catalytic degradation capability of the Fenton process [49].
475 Moreover, the efficient mineralization of the cefazolin improves the potential of the effluent to
476 be treated by the subsequent biological system as a post-treatment method with
477 environmentally friendly effluent. However, the degradation of the target organic compound
478 may result in the formation of unknown organic and inorganic compounds. Thus, GC-MS
479 analysis was carried out to identify the intermediate byproducts generated during the
480 destruction of cefazolin through the CuFeNLDH-CNTs/EF process. The results of GC-MS
481 analysis are displayed in Table 3. According to the byproducts listed in Table 3, cefazolin can
482 be degraded by cleavage of C-S, N=N, N-N, C-N and C-C bonds. In the first step, the parent
483 molecule was disintegrated to hydroxylated cyclic hydrocarbons such as 2-(3-isopropenyl-4-
484 methyl-4-vinylcyclohexyl)-2-propanol, (NE)-N-(2-methyl-5-prop-1-en-2-ylcyclohex-2-en-1-
485 ylidene) hydroxylamine and 2-ethylcyclohexan-1-ol. In the next step, (2E)-3,7-dimethylocta-
486 2,6-dien-1-ol, Octan-4-ol and pentan-2-ol were produced as hydroxylated aliphatic compounds
487 derived from the ring cleavage. Then, various short-chain aliphatic carboxylic acids such as
488 propan-2-ol, 1,1-bis(methylsulfonyl)ethane, acetic acid, 2-hydroxyacetaldehyde and acetamide
489 were produced as the final intermediates. According to the results reported by Le et al., the
490 formation of short-chain aliphatic compounds can result in the detoxification of solution [60].
491 Using evolution of inhibition ratio, they have demonstrated that the toxicity is closely

492 associated with the existence of aromatic compounds at the early step of the degradation
493 process rather than short-chain aliphatic compounds detected at the end of the EF process which
494 have insignificant toxicity. Eventually, all of these compounds could be converted to carbon
495 dioxide and water as the final products to achieve mineralization [61]. The AAS technique was
496 also applied to determine the total concentration of Fe and Cu ions dissolved in the cefazolin-
497 contained solution during the CuFeNLDH-CNTs/EF process. The AAS analysis results
498 revealed the release of Fe (0.21 mg/L) and Cu (0.34 mg/L) ions from the modified graphite
499 cathode into the solution during the treatment process. The stability of the CuFeNLDH-CNTs-
500 coated graphite cathode was also investigated by performing ten consecutive experiments.
501 After each experiment, the cathode was washed with distilled water and dried at room
502 temperature. Then, the next experiment was performed under the same experimental
503 conditions. As presented in Fig. S7, there is no remarkable decrement in the performance of
504 CuFeNLDH-CNTs-coated graphite cathode after ten experiments, confirming high stability of
505 the CuFeNLDH-CNTs-modified cathode for the EF process. No more than 4.0% reduction in
506 the removal efficiency of cefazolin was observed at the end of tenth run. This improves the
507 potential of the treatment process to be used in full-scale applications with considerable cost-
508 effectiveness.

509

510 **4. Conclusion**

511 CNTs-incorporated CuFeNLDH was immobilized on the surface of the graphite plate to be
512 efficiently applied as a porous cathode for the degradation of cefazolin antibiotic through the
513 EF process. Characterization analyses proved the superior structure of CuFeNLDH/CNTs-
514 coated graphite in comparison with both bare and CNTs-coated cathodes for the reduction of
515 oxygen molecules to hydrogen peroxide as well as decomposition of hydrogen peroxide to $\cdot\text{OH}$

516 radicals. Increasing the current intensity and supporting electrolyte concentration led to the
517 enhanced destruction of cefazolin through the modified EF process. Conversely, increasing the
518 initial cefazolin concentration along with increasing solution pH resulted in decreased
519 decomposition efficiency. Evaluation of the efficiency of the treatment process in the presence
520 of radical scavenging compounds demonstrated the major role of free oxidizing radicals,
521 especially $\cdot\text{OH}$ radicals, in the degradation of the target contaminant. These results also showed
522 the high potential of the treatment process to be operated under real conditions. The treatment
523 process had relatively high potential in mineralization of the bio-refractory antibiotic with the
524 release of low amounts of Cu and Fe ions into the bulk solution. The results of GC-MS analysis
525 confirmed the acceptable progress in the conversion of parent compound into the intermediates
526 with low molecular weight and simple structure. Overall, the EF process equipped with
527 CuFeNLDH/CNTs-coated graphite cathode can be utilized as one of the promising Fenton-
528 based AOPs for the decontamination of antibiotic-polluted water streams before being
529 discharged into various ecosystems.

530

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727 **Figures captions**

728 **Fig. 1.** SEM images of CuFeNLDH (a-d), CNTs (e-h), CuFeNLDH-CNTs (i-l) and
729 CuFeNLDH-CNTs-coated graphite cathode (m-p).

730 **Fig. 2.** HR-TEM images of CuFeNLDH (a and b) and CuFeNLDH-CNTs (c and d), along with
731 thickness (e) and width (f) size distribution plots of CuFeNLDH nanosheets.

732 **Fig. 3.** XRD patterns of CuFeNLDH (a) CuFeNLDH-CNTs (b) and CuFeNLDH-CNTs
733 modified graphite (c).

734 **Fig. 4.** XPS spectra of (a) CuFeNLDH, (b) CuFeNLDH-CNTs and (c) CuFeNLDH-CNTs-
735 coated graphite; together with high resolution Fe 2p (d-f), Cu 2p (g-i) and O 1s (j-l) XPS spectra
736 of CuFeNLDH, CuFeNLDH-CNTs and CuFeNLDH-CNTs-coated graphite samples.

737 **Fig. 5.** CV scans in N₂- saturated (a) and (b) O₂-saturated solutions and LSV (b) curves for the
738 bare graphite and CuFeNLDH/CNTs-modified graphite cathodes.

739 **Fig. 6.** (a) Comparison of various graphite cathodes, including graphite/NLDH-CNTs (0.10 g),
740 graphite/NLDH-CNTs (0.05 g), graphite/NLDH-CNTs (0.15 g) and graphite/CNTs (0.10 g)
741 for the degradation of cefazolin through EF process; along with the (b) comparison of the
742 amount of H₂O₂ molecules generated on the surface of graphite/CNTs, bare graphite,
743 graphite/NLDH-CNTs (0.05 g) , graphite/NLDH-CNTs (0.10 g) and graphite/NLDH-CNTs
744 (0.15 g) electrodes (Experimental conditions: pH = 6, [cefazolin]₀ = 20.0 mg/L, current = 300.0
745 mA, [Na₂SO₄] = 50.0 mmol/L and air flow rate = 10.0 L/h).

746 **Fig. 7.** (a) The effect of solution pH ([cefazolin]₀ = 20.0 mg/L, current = 400.0 mA, [Na₂SO₄]
747 = 50.0 mmol/L and air flow = 10.0 L/h), (b) applied current (pH = 6.0, [cefazolin]₀ = 20.0
748 mg/L, [Na₂SO₄] = 50.0 mol/L and air flow = 10.0 L/h), (c) initial concentration of cefazolin
749 (pH = 6.0, current = 300.0 mA, [Na₂SO₄] = 50.0 mmol/L and air flow = 10.0 L/h), and (d)
750 electrolyte concentration (pH = 6.0, [cefazolin]₀ = 20.0 mg/L, current = 300.0 mA and air flow
751 = 10.0 L/h) on the degradation of cefazolin through CuFeNLDH-CNTs/EF process.

752 **Fig. 8.** Effects of ethanol (a), benzoquinone (b), and carbonate ions (c) on the degradation of
753 cefazolin by the CuFeNLDH-CNTs/EF process. Experimental conditions: pH = 6, [cefazolin]₀
754 = 20.0 mg/L, current = 300.0 mA, [Na₂SO₄] = 50.0 mmol/L, air flow rate = 10.0 L/h and
755 [scavenger] = 5.0-15.0 mmol/L.

756 **Fig. 9.** Effect of gas injection (air, O₂, O₃, and Ar) on the degradation of cefazolin by the
757 CuFeNLDH-CNTs/EF process. Experimental conditions: pH = 6.0, [cefazolin]₀ = 20.0 mg/L,
758 current = 300.0 mA, [Na₂SO₄] = 50.0 mmol/L, gas flow rate = 10.0 L/h.

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781 **Research highlights**

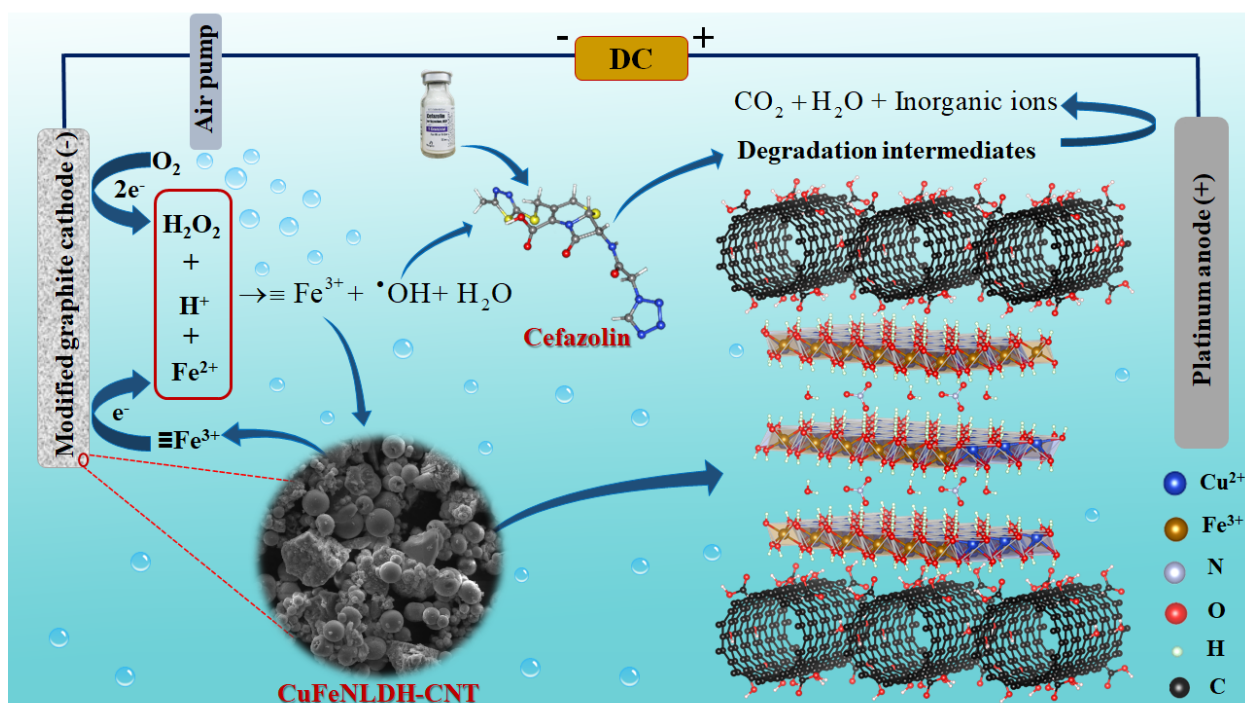
- 782 • Preparation of CuFeNLDH-CNTs incorporated graphite cathode.
- 783 • Study of the performance of CuFeNLDH-CNTs attached cathode in electro-Fenton process.
- 784 • Achievement of the highest cefazolin degradation through CuFeNLDH-CNTs/EF process.
- 785 • Evaluation of the effect of operational parameters on the degradation of cefazolin.
- 786 • Identification of degradation intermediates using GC-MS analysis.

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789 **Graphical abstract**

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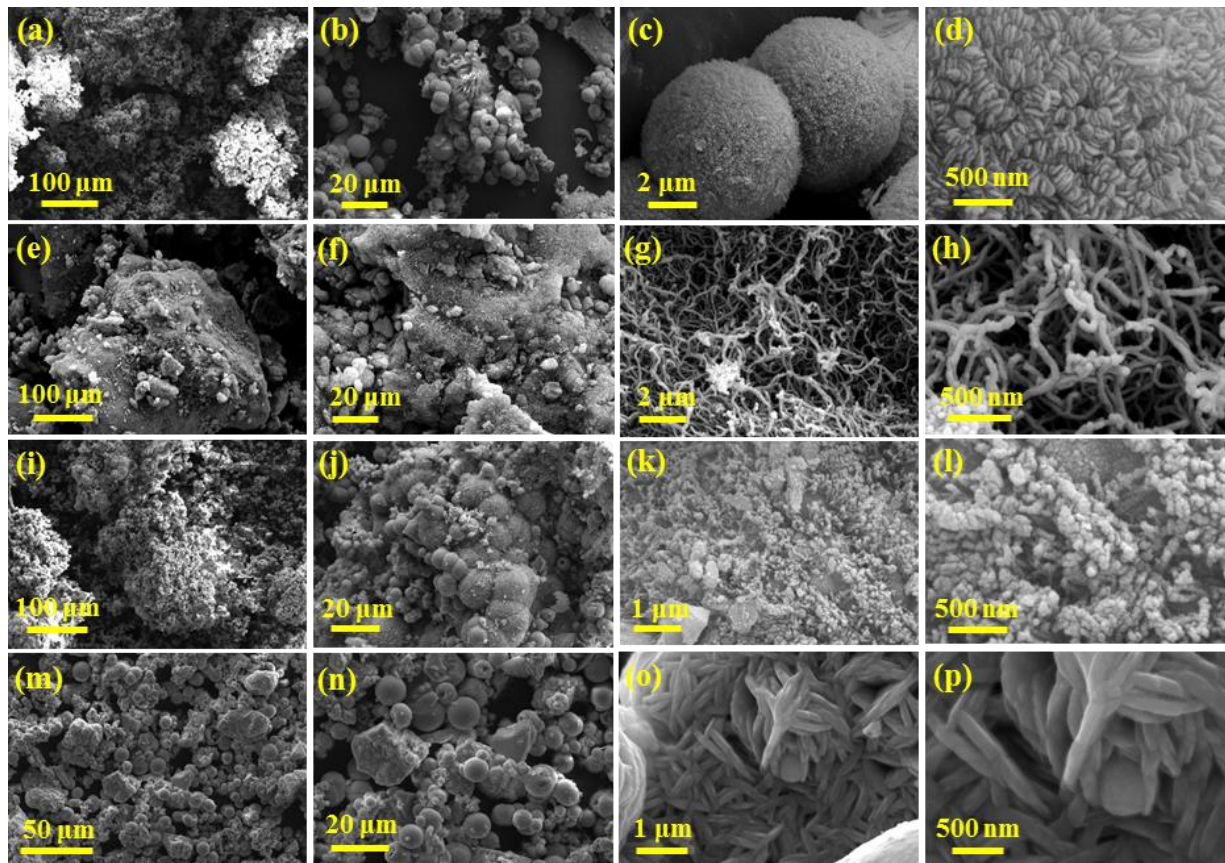
Figures

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803 **Fig. 1.** SEM images of CuFeNLDH (a-d), CNTs (e-h), CuFeNLDH-CNTs (i-l) and
804 CuFeNLDH-CNTs-coated graphite cathode (m-p).

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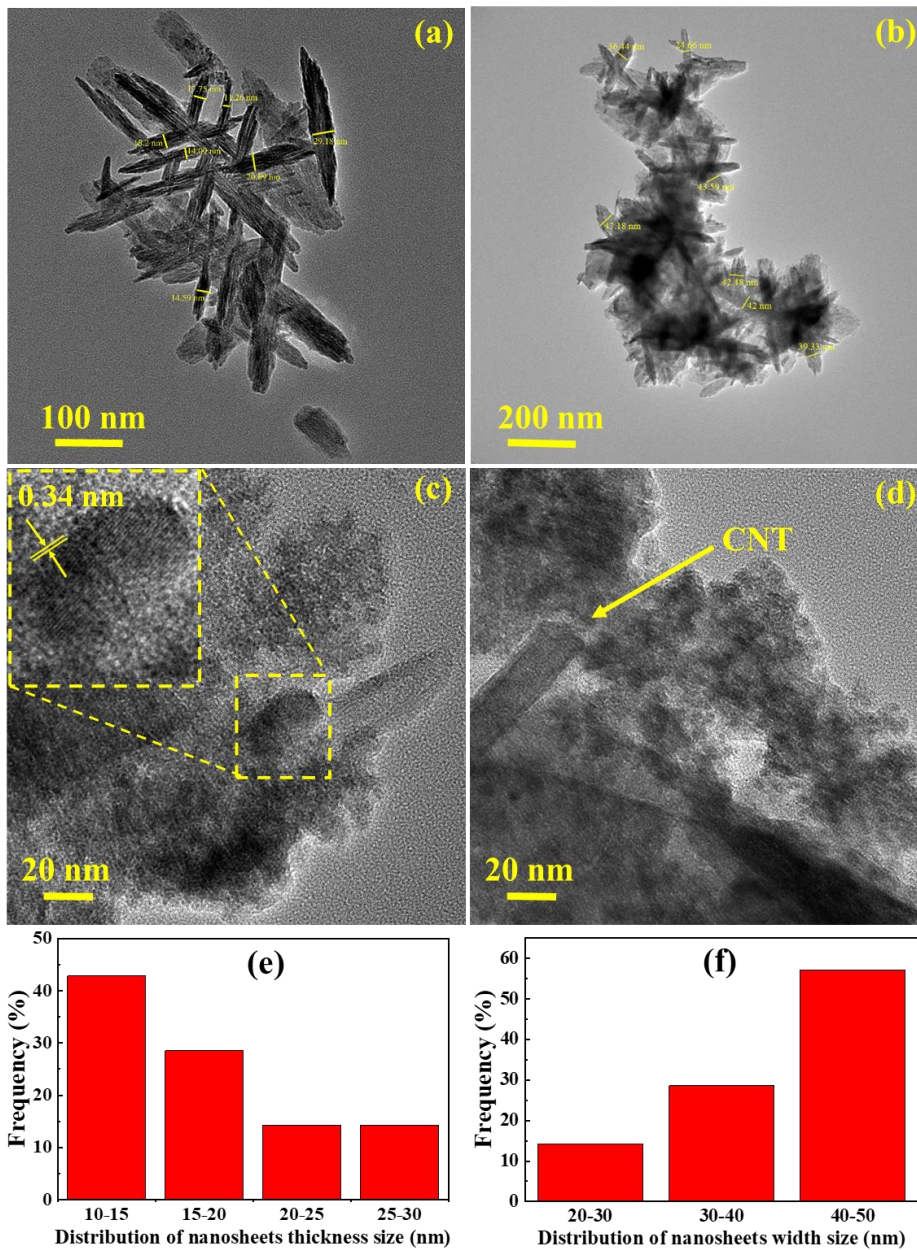
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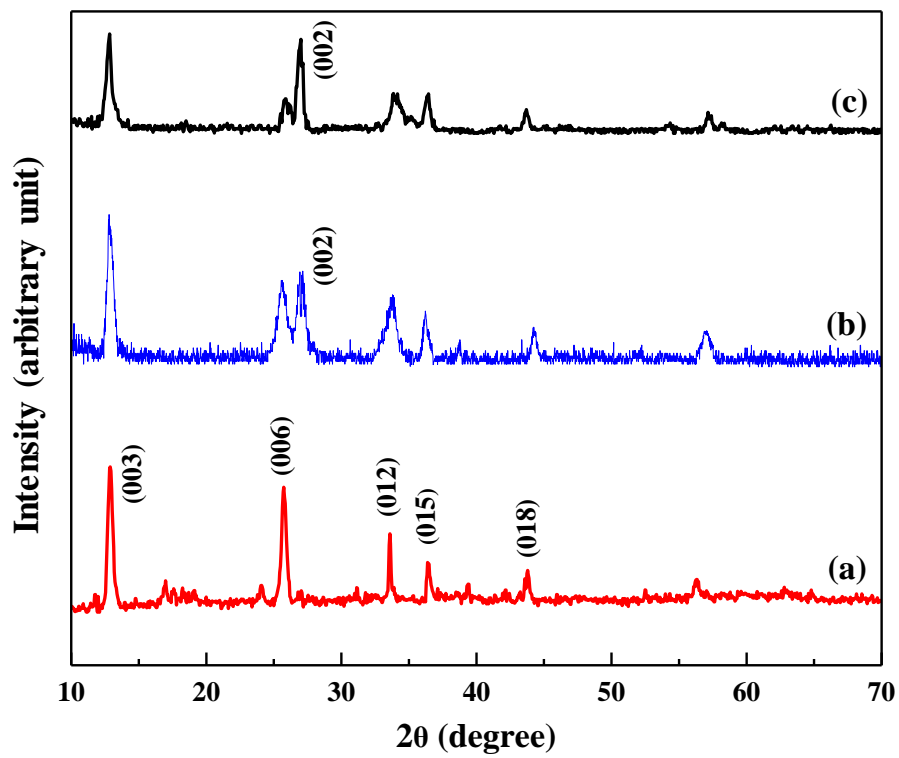
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Fig. 2. HR-TEM images of CuFeNLDH (a and b) and CuFeNLDH-CNTs (c and d), along with thickness (e) and width (f) size distribution plots of CuFeNLDH nanosheets.

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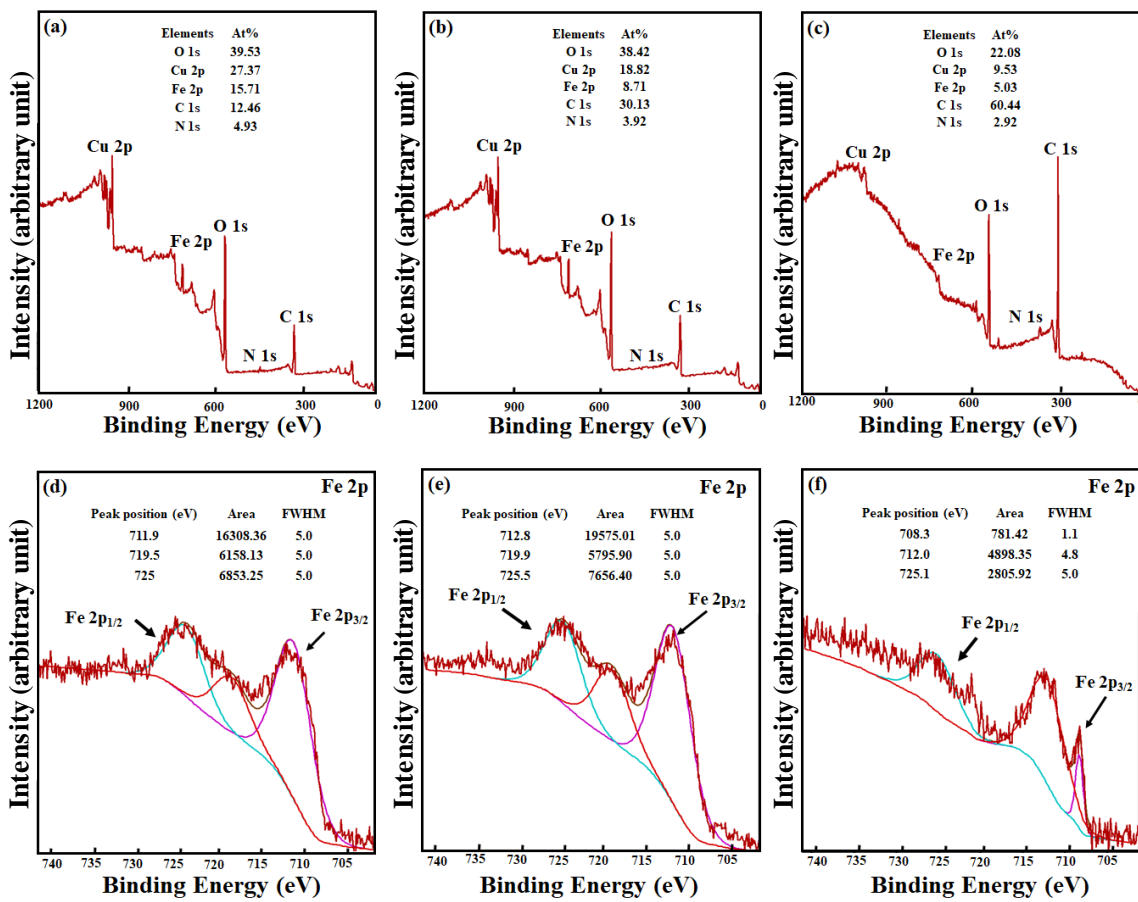


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Fig. 3. XRD patterns of CuFeNLDH (a) CuFeNLDH-CNTs (b) and CuFeNLDH-CNTs modified graphite (c).

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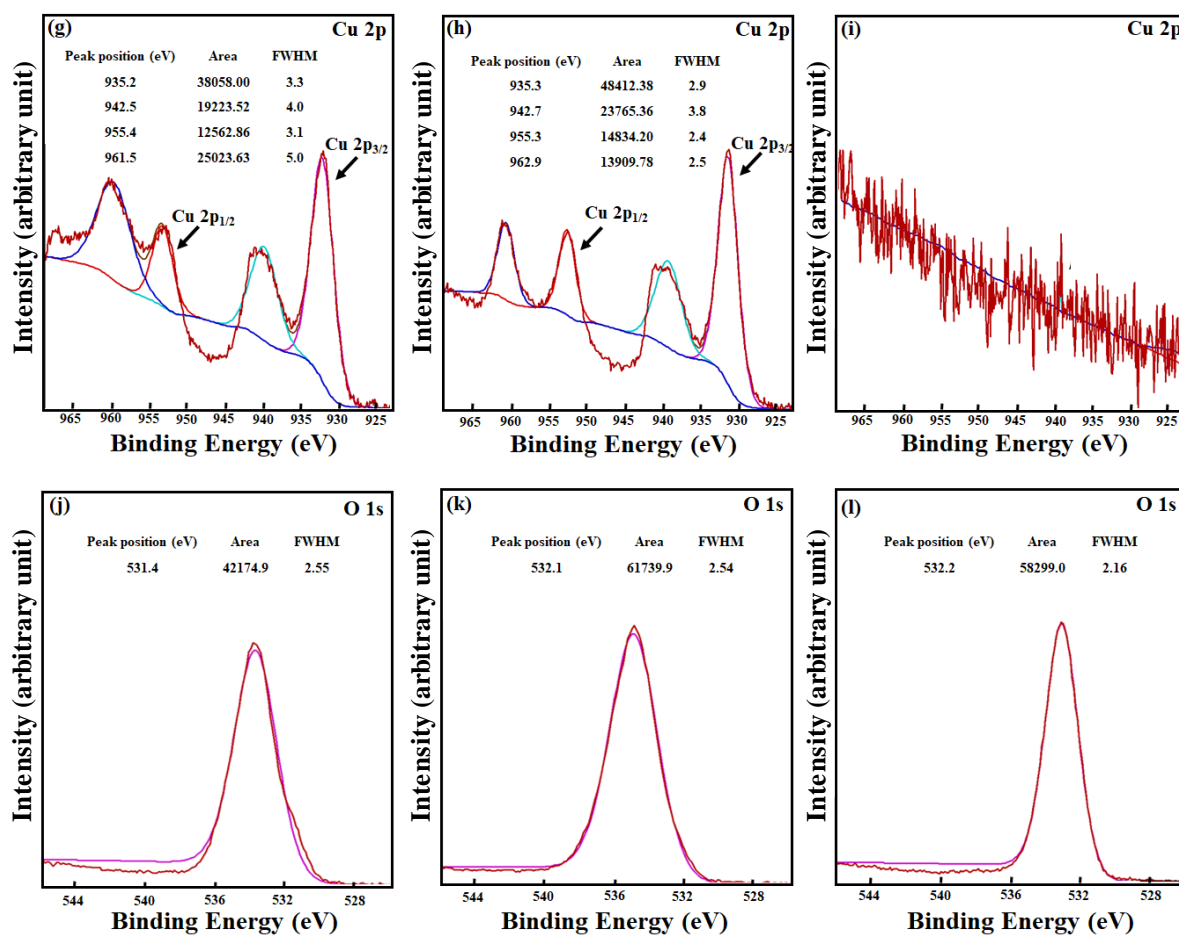
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Fig. 4 (a-f)

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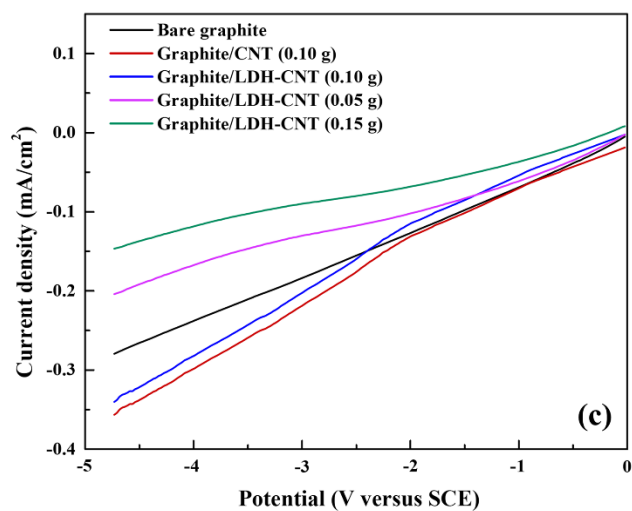
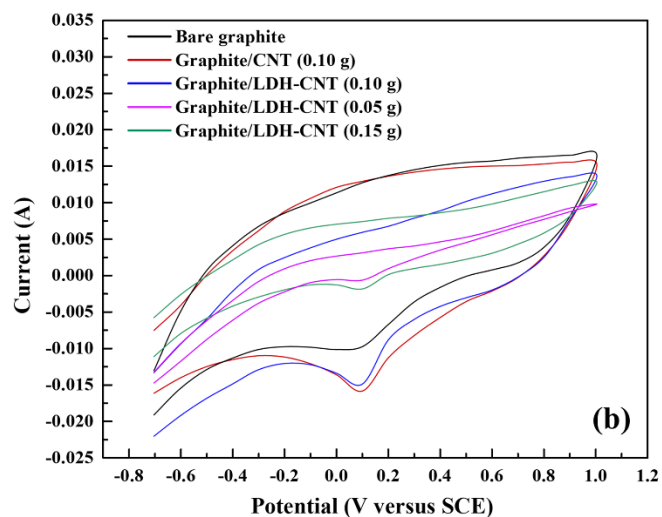
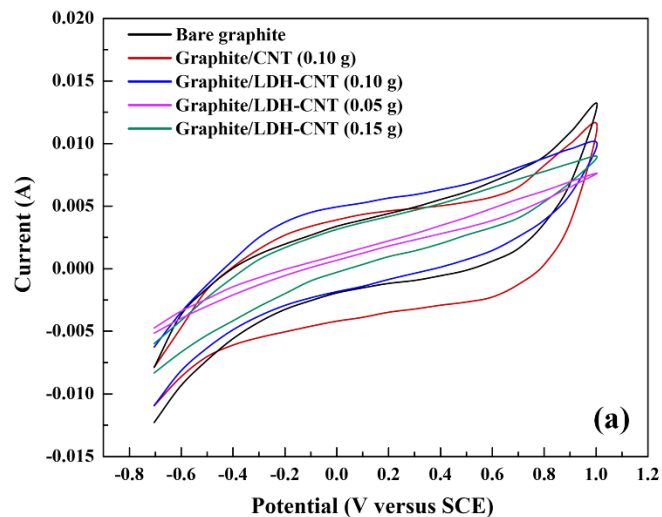


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Fig. 4 (g-l)

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Fig. 4. XPS spectra of (a) CuFeNLDH, (b) CuFeNLDH-CNTs and (c) CuFeNLDH-CNTs-coated graphite; together with high resolution Fe 2p (d-f), Cu 2p (g-i) and O 1s (j-l) XPS spectra of CuFeNLDH, CuFeNLDH-CNTs and CuFeNLDH-CNTs-coated graphite samples.



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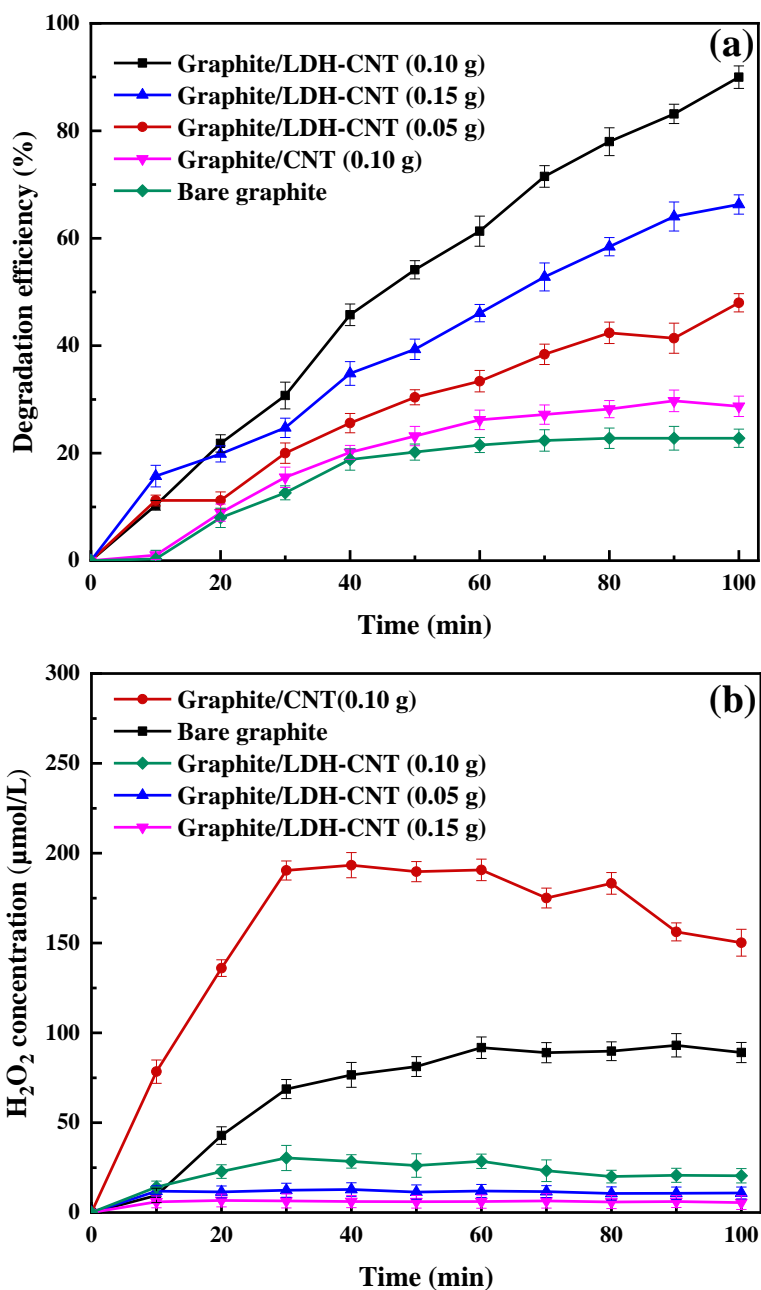
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867 **Fig. 5.** CV scans in N_2 -saturated (a) and O_2 -saturated (b) solutions and LSV

868 curves (c) for the bare graphite and CuFeNLDH/CNTs-modified graphite

869 cathodes.

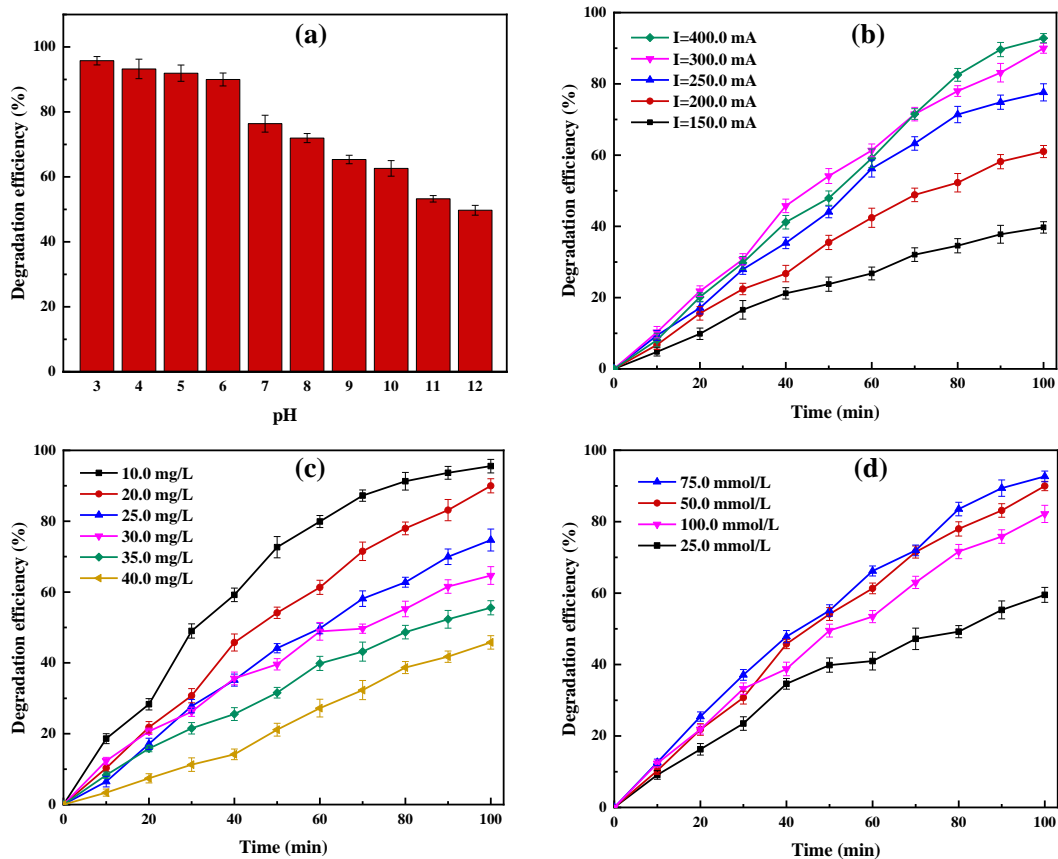
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873 **Fig. 6.** (a) Comparison of various graphite cathodes, including graphite/NLDH-CNTs (0.10
874 g), graphite/NLDH-CNTs (0.05 g), graphite/NLDH-CNTs (0.15 g) and graphite/CNTs (0.10
875 g) for the degradation of cefazolin through EF process; along with the (b) comparison of the
876 amount of H₂O₂ molecules generated on the surface of graphite/CNTs, bare graphite,
877 graphite/NLDH-CNTs (0.05 g), graphite/NLDH-CNTs (0.10 g) and graphite/NLDH-CNTs
878 (0.15 g) electrodes (Experimental conditions: pH = 6, [cefazolin]₀ = 20.0 mg/L, current =
879 300.0 mA, [Na₂SO₄] = 50.0 mmol/L and air flow rate = 10.0 L/h).

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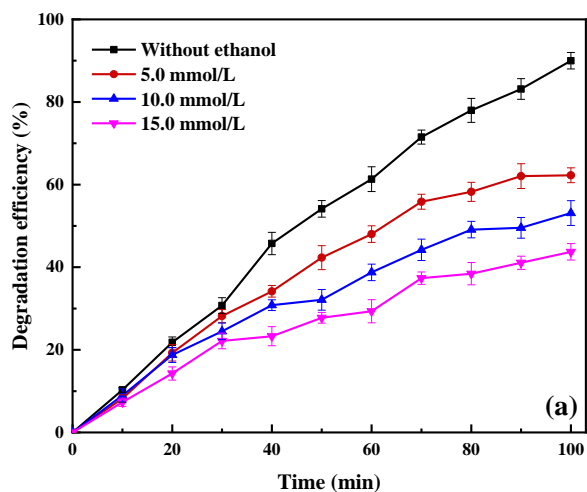
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882 **Fig. 7.** (a) The effect of solution pH ($[\text{cefazolin}]_0 = 20.0 \text{ mg/L}$, current = 400.0 mA, $[\text{Na}_2\text{SO}_4]$
 883 = 50.0 mmol/L and air flow = 10.0 L/h), (b) applied current (pH = 6.0, $[\text{cefazolin}]_0 = 20.0$
 884 mg/L, $[\text{Na}_2\text{SO}_4] = 50.0 \text{ mol/L}$ and air flow = 10.0 L/h), (c) initial concentration of cefazolin
 885 (pH = 6.0, current = 300.0 mA, $[\text{Na}_2\text{SO}_4] = 50.0 \text{ mmol/L}$ and air flow = 10.0 L/h), and (d)
 886 electrolyte concentration (pH = 6.0, $[\text{cefazolin}]_0 = 20.0 \text{ mg/L}$, current = 300.0 mA and air
 887 flow = 10.0 L/h) on the degradation of cefazolin through CuFeNLDH-CNTs/EF process.

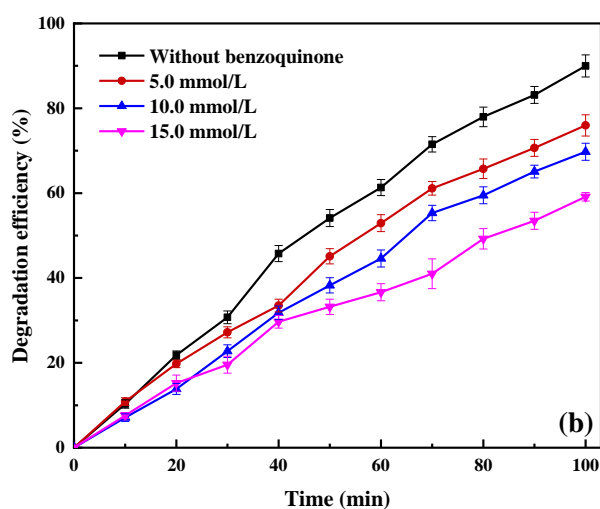
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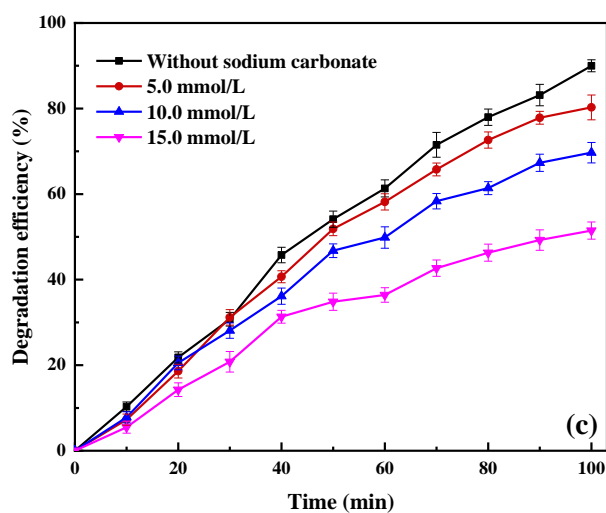
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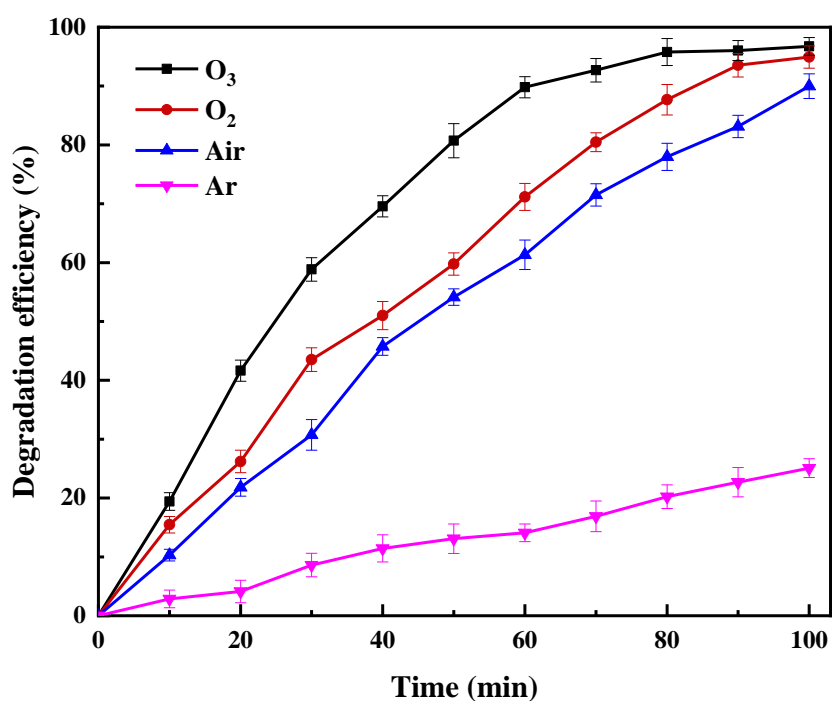
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894 **Fig. 8.** Effects of ethanol (a), benzoquinone (b), and carbonate ions (c) on the degradation of
 895 cefazolin by the CuFeNLDH-CNTs/EF process. Experimental conditions: pH = 6,
 896 [cefazolin]₀ = 20.0 mg/L, current = 300.0 mA, [Na₂SO₄] = 50.0 mmol/L, air flow rate = 10.0
 897 L/h and [scavenger] = 5.0-15.0 mmol/L.
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912 **Fig. 9.** Effect of gas injection (air, O₂, O₃, and Ar) on the degradation of cefazolin by the
913 CuFeNLDH-CNTs/EF process. Experimental conditions: pH = 6.0, [cefazolin]₀ = 20.0 mg/L,
914 current = 300.0 mA, [Na₂SO₄] = 50.0 mmol/L, gas flow rate = 10.0 L/h.
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943 **Table 2.** Identified intermediate byproducts generated during the degradation of cefazolin by
 944 the heterogeneous EF process. Experimental conditions: pH = 6.0, current = 300.0 mA,
 945 [cefazolin]₀ = 20.0 mg/L, [Na₂SO₄] = 50.0 mmol/L, and air flow rate = 10.0 L/h.

No.	Compound name	Structure	Retention time (min)	Main fragments
1	2-(4-methyl-3-(prop-1-en-2-yl)-4-vinylcyclohexyl)propan-2-ol		15.678	69, 75, 82, 93, 148
2	(2E)-3,7-dimethylocta-2,6-dien-1-ol		12.216	68, 69, 121, 148
3	2-Cyclohexen-1-one, 2-methyl-5-(1-methylethenyl)-, oxime		10.163	54, 82, 93, 108, 207
4	Propan-2-ol		7.167	59, 73, 75, 147, 187
5	Pentan-2-ol		7.03	59, 75, 147, 187
6	Octan-4-ol		7.012	73, 75, 147
7	1,1-bis(methylthio)ethane		6.912	59, 73, 75, 147, 149
8	2-Ethylcyclohexanol		3.938	68, 69, 93, 148
9	Acetic acid		3.805	59, 75, 76, 116
10	2-Hydroxyacetaldehyde		3.339	73, 75, 76, 116

11	Acetamide		3.150	59, 73, 75 , 76, 116
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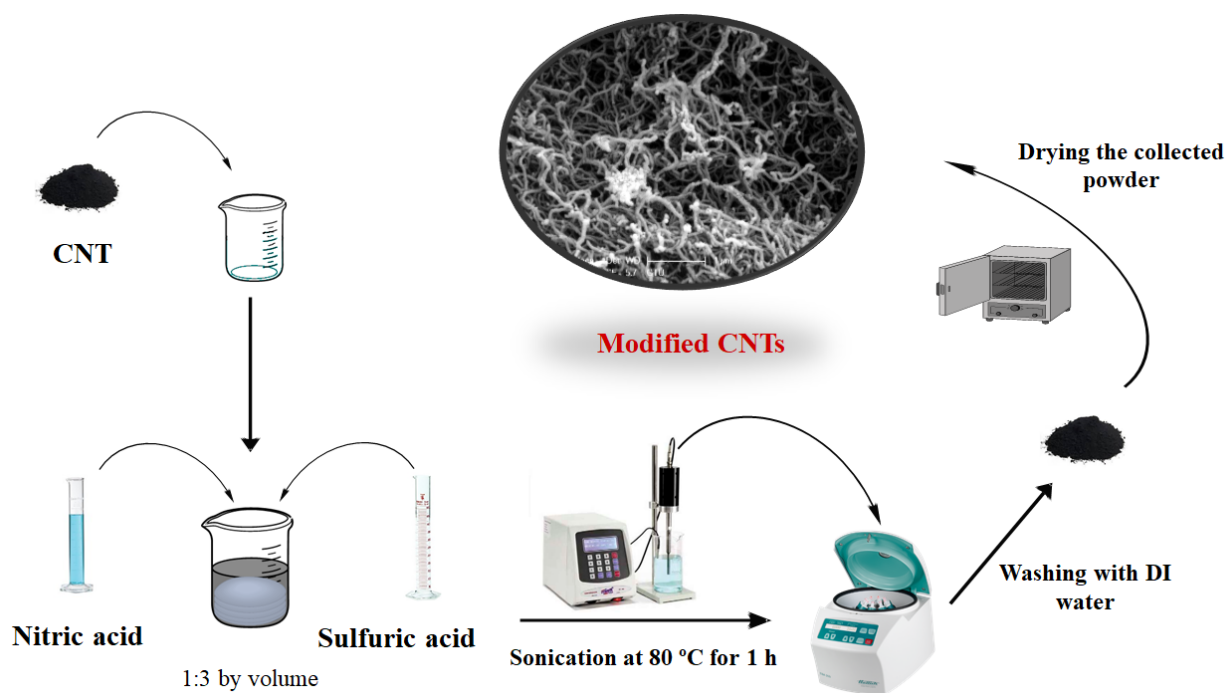
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Supplementary data

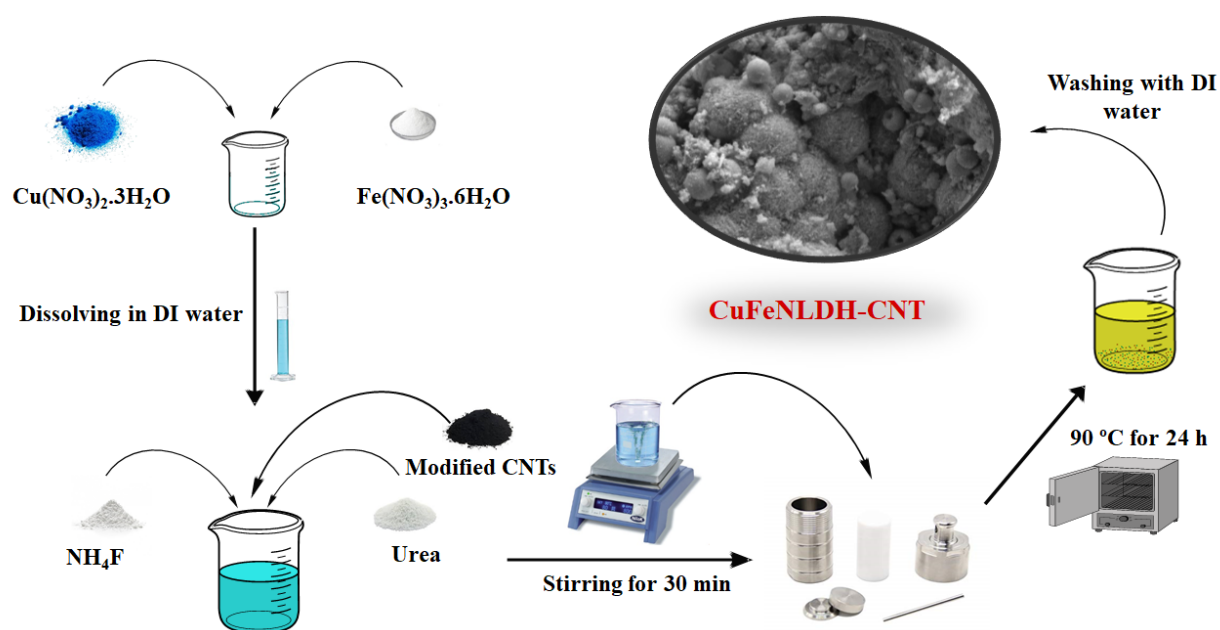
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Fig. S1. Schematic design for the modification of CNTs.

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995 **Fig. S2.** Schematic diagram for synthesis of CuFeNLDH-CNTs.

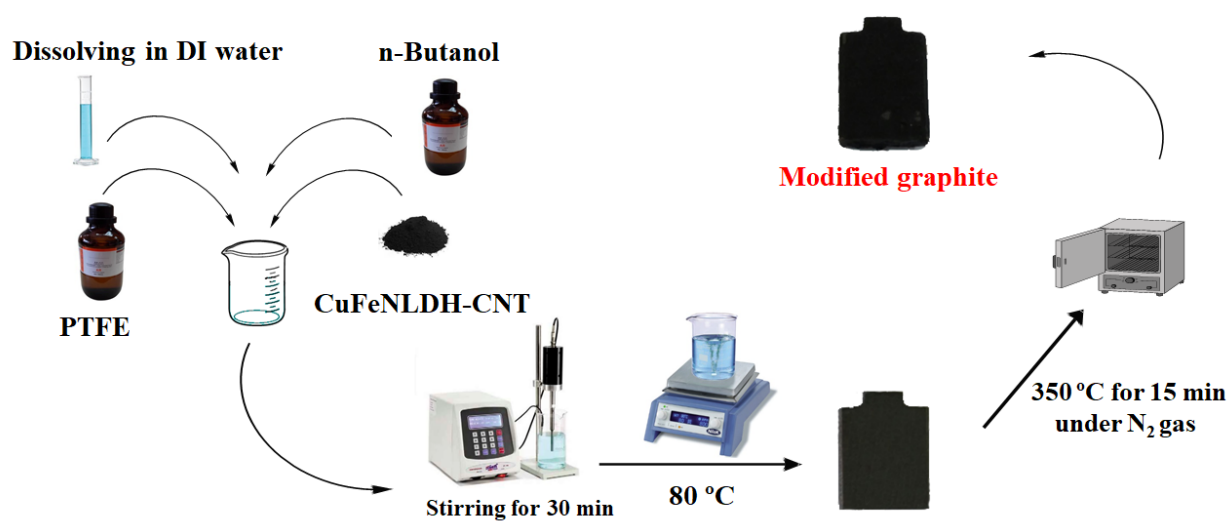
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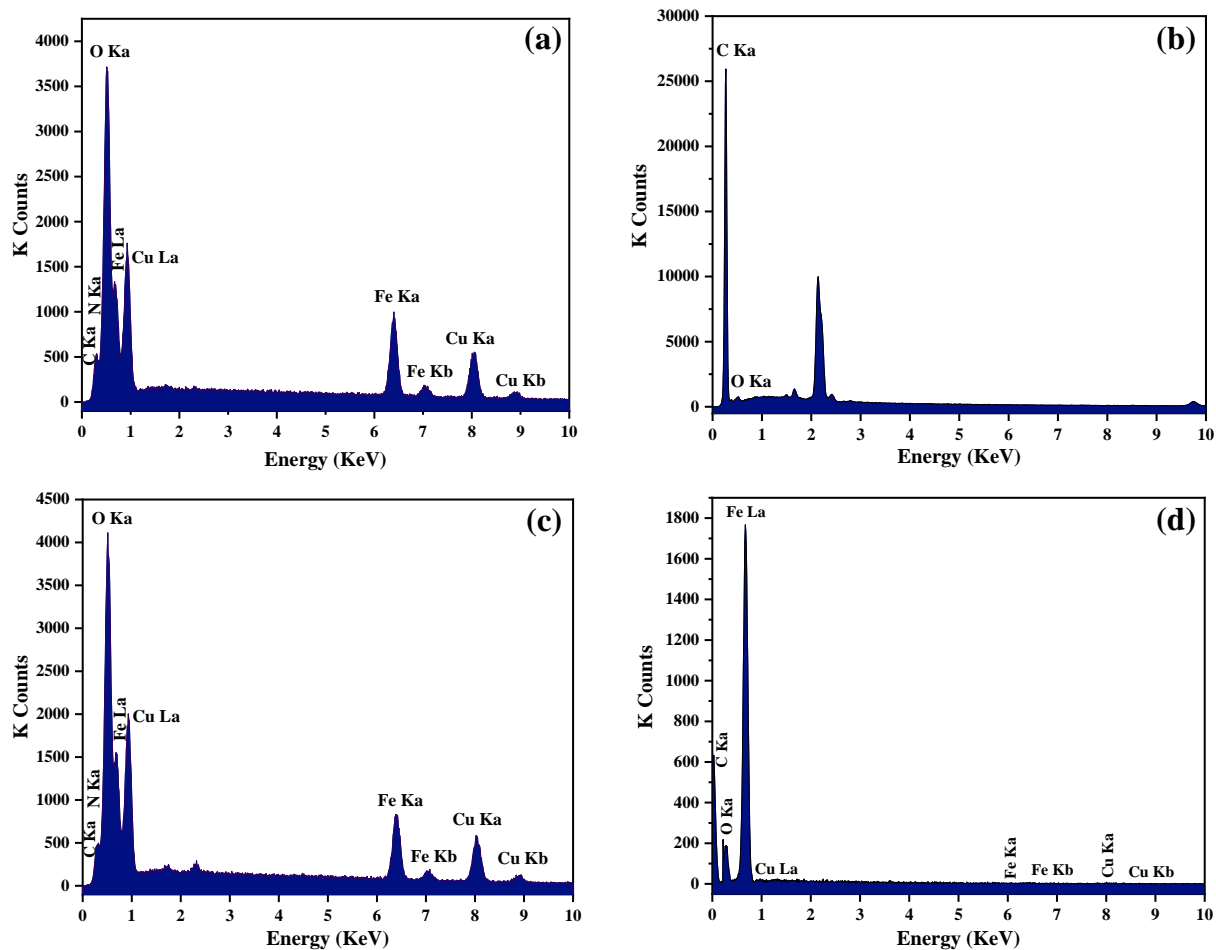
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Fig. S3. Schematic diagram for immobilization of CuFeNLDH-CNTs nanocomposite on the surface of graphite plate.

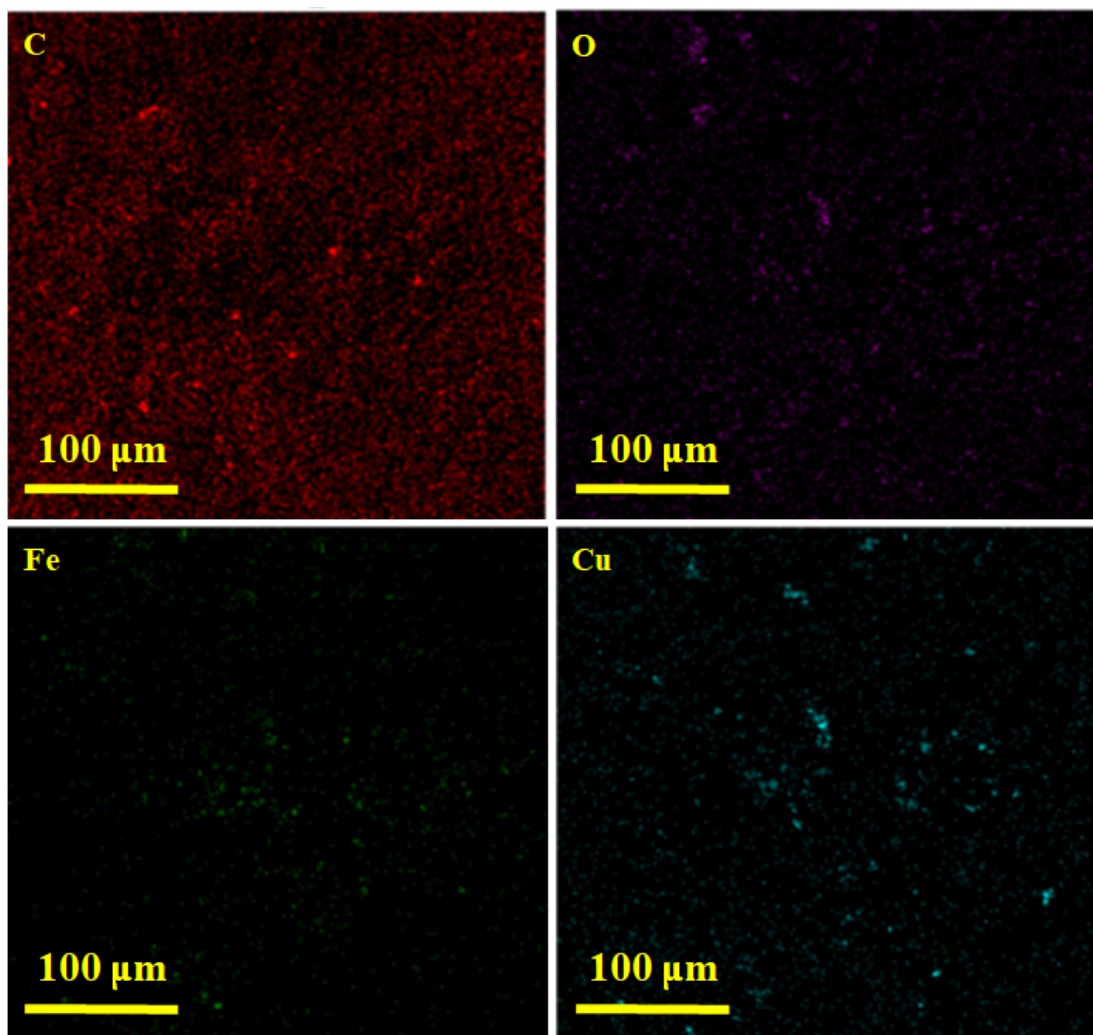
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Fig. S4. EDX spectra of CuFeNLDH (a) CNTs (b), CuFeNLDH-CNTs (c) and modified graphite (d).

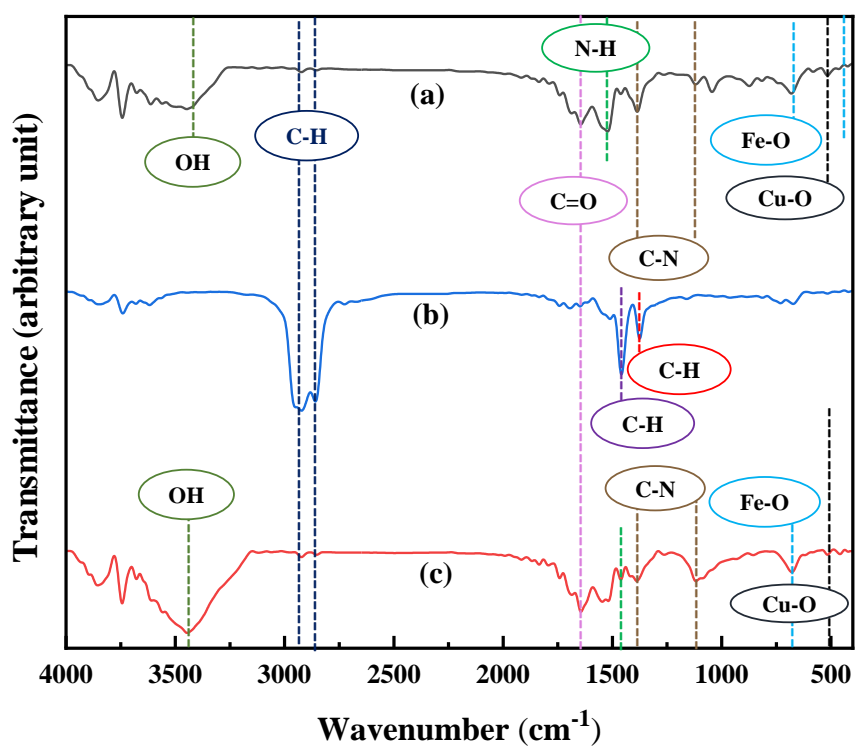
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Fig. S5. Elemental mapping images of CuFeNLDH-CNTs-coated -coated graphite cathode.

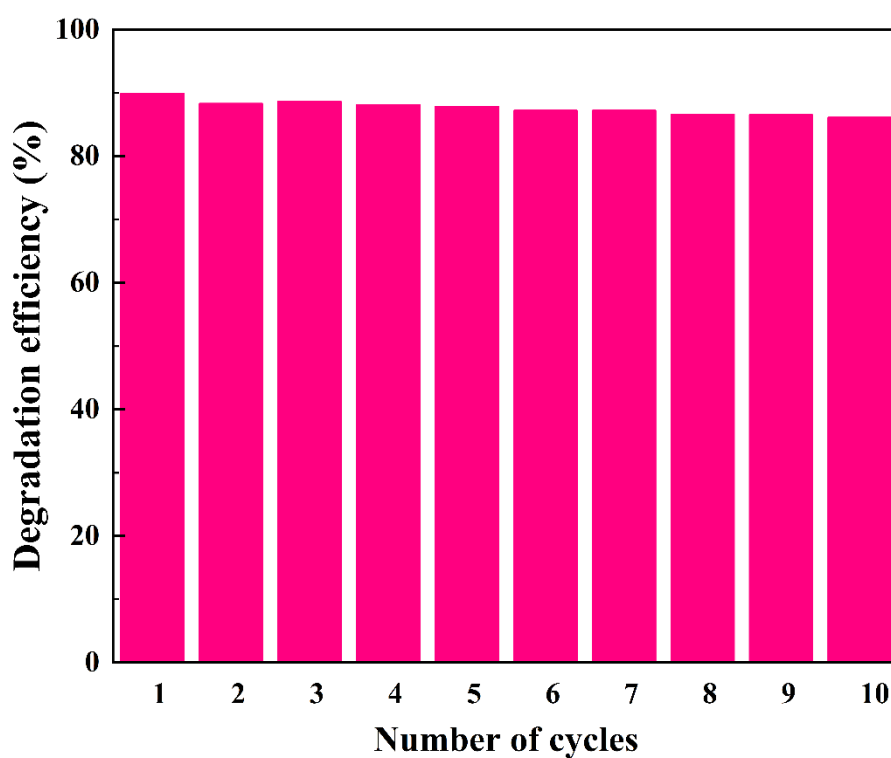
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Fig. S6. FT-IR spectra of CuFeNLDH (a) CNTs (b) and CuFeNLDH/CNTs (c).

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Fig. S7. Cyclic stability of CuFeNLDH-CNTs-coated graphite cathode for CFZ degradation through EF process; Experimental condition: pH = 6, [cefazolin]₀ = 20.0 mg/L, current = 300.0 mA, [Na₂SO₄] = 0.05 mol/L and air flow rate = 10.0 L/h.