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# A comparative study of ceramics nanoparticles synthesized for antibiotic removal: Catalysis characterization and photocatalytic performances modeling

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## Abstract

The heterogeneous photocatalysis process has been known to provide significant levels of degradation and mineralization of emerging contaminants including antibiotics. For that, nanoparticles  $\text{CuCr}_2\text{O}_4$  (CCO) ceramics were successfully prepared via sol-gel (SG) and co-precipitation (CP) methods to obtain spinel with desired structural features and properties and also to improve the photocatalytic performances. The CCO crystallite phase was produced at 750 °C all ceramics, disregarding the synthesis route. CCO physical and chemical properties were checked by X-ray diffraction (XRD) with Rietveld refinement, Brunauer Emmett Teller (BET), Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Diffuse Reflectance Solid (DRS). The XRD patterns demonstrated that the synthesized catalysts displayed a small crystallite size between 17.45 and 26.24 nm for SG and 20.97 to 36.86 nm for the  $\text{CCO}_{\text{CP}}$  samples. The observation by SEM and TEM of the nanopowders showed a typical morphology with comparable particle sizes for both synthesized routes (20–30 nm). SG agglomeration rates were higher, and particles

33 stick together more efficiently considering the CP method, while the CCO<sub>CP</sub> method  
34 led to a more significant porosity.

35 Their photocatalytic and adsorption performances were examined for Cefaclor (CFC)  
36 removal chosen as a target pharmaceutical contaminant in water. The results  
37 obtained by the methods differed since nanoparticles prepared by SG led to high  
38 photocatalytic activity. In contrast, a high CFC adsorption was observed for those  
39 prepared via the CP method, and that agreed with the findings of the characterization  
40 analysis. The Kinetics of the adsorption process was found to follow the pseudo-  
41 second-order rate law. In contrast, the data of the photodegradation process were  
42 further found to comply with the Lagergren kinetic law. Nevertheless, the global  
43 reaction rate is probably controlled by the intra-particle diffusion of CFC, regardless  
44 of the elimination process.

45

46 **Keywords:** Ceramics nanoparticles, Co-precipitation, Sol-gel processes,  
47 Photocatalysis, Adsorption, Kinetic modeling.

48

## 49 1. Introduction

50 Water is definitely our planet's most important natural resource, and it is necessary  
51 for all species in our lives. Approximately 71 % of the surface of the earth is wrapped  
52 by water, while the oceans occupy about 96.5 % of the water resources (Kümmerer  
53 2009). In the context of icecaps and frozen seas, freshwater constitutes only 2.5 % of  
54 the polar premises and rivers, lakes and reservoirs only 0.3 % of the global water  
55 resources. Despite the lack of fresh water on earth, it is constantly contaminated with  
56 various chemical contaminants such as drugs (Kaczala and E. Blum 2015).

57 Various medicinal compounds have sullied the aqueous environment in recent  
58 years, including antibiotics that need special attention because of their large use in  
59 human and veterinary medicine (Lalouckova and Skrivanova 2019), as well as in  
60 improving feed quality and growth levels in the livestock and poultry industries. In  
61 addition, antibiotics are the main concern of researchers all over the world if  
62 compared to the other categories of pharmaceutical products because of their  
63 increasing aquatic toxicity and nonbiodegradability in the environment (Mostafaloo et  
64 al. 2019; Aissani et al. 2020). Generally, antibiotics are present at amounts ranging  
65 from ng/L to µg/L in treated wastewater (Ikhlef-Taguelmimt et al. 2020; Kadji et al.

66 2020). Even at very low amounts, the existence of these substances in water  
67 resources, enhances bacterial resistance (Shooshtari and Ghazi 2017).

68 A target antibiotic example is Cefaclor (CFC) belonging to the beta-lactam group,  
69 second-generation cephalosporin with antibacterial activity. Cefaclor is (6R,7R) -7-  
70 [[[2R)-2-amino-2-phenylacetyl]amino]-3-chloro-8-oxo-5-thia-1 azabicyclo [4.2.0] oct-  
71 2-ene-2-carboxylic acid with molecular formula  $C_{15}H_{14}ClN_3O_4S$ . Also, it is a  
72 cephalosporin bearing chloro and (R)-2-amino-2-phenylacetamido groups at  
73 positions 3 and 7, respectively; the above described molecular structure is displayed  
74 in Figure S.1. It has a role as an antibacterial and allergen drugs. To our knowledge,  
75 no study has been made yet concerning the photocatalyst degradation of cefaclor.

76 Conventional methods cannot effectively eliminate antibiotic residues due to  
77 antibacterial nature (Chen and Huang 2010; Li and Zhang 2010; Gao et al. 2012). In  
78 this respect, Advanced Oxidation Processes (AOPs) have proven to be a suitable  
79 alternative for the rapid destruction of recalcitrant and non-biodegradable compounds  
80 in contaminated waters (Lou et al. 2017; Aboudalle et al. 2018; Kamagate et al.  
81 2018; Yahiaoui et al. 2018; Kadji et al. 2020). The heterogeneous photocatalysis  
82 process in particular has been successfully used to degrade different types of  
83 pharmaceutical drugs and organic compounds (Zhu et al. 2013; Aissani et al. 2018,  
84 2020; Hou et al. 2019; Ikhlef-Taguelmimt et al. 2020; Shan et al. 2020). our previous  
85 study showed that  $CuCr_2O_4$  (CCO) photocatalyst had a good photocatalytic reduction  
86 of Cr(VI) (Lahmar et al. 2012). Also, CCO has been shown a significant degradation  
87 activity for removal of organic and antibiotics compounds (Akhundi and Habibi-  
88 Yangjeh 2017; Hariganesh et al. 2020). For that, CCO was considered and It was  
89 synthesized by different routes.

90 There is a considerable amount of research concentrating on the preparation  
91 methods to enhance the photo-catalytical properties as they have been found to have  
92 a strong effect on the semiconductor's crystallinity (Santhanam and Rambabu 2010;  
93 Kafshgari et al. 2019). The facile method for preparing CCO ceramic involves mixing  
94 copper nitrate and chromium nitrate in a 1:2 molar ratio and then calcining at  $750\text{ }^\circ\text{C}$   
95 for 6 hours (Acharyya et al. 2015). Wet chemical methods like sol-gel (Geng et al.  
96 2012), co-precipitation (Hu et al. 2011) and hydrothermal (Mobini et al. 2017)  
97 methods are auspicious routes for yielding high purity single-phase CCO at  
98 approximately low temperatures, although certain inconveniences exist. For example,

99 hydrothermal synthesis needs the usage of an autoclave with pressures of about 70-  
100 175 MPa (Ramanujam et al. 2014), whilst synthesized combustion powders lead to  
101 chemical inhomogeneity and particles agglomeration because of strong local heating  
102 (Devi et al. 2002; Ramanujam et al. 2014; Das et al. 2018). Nevertheless, the  
103 synthesis of sol-gel and co-precipitation may be inexpensive methods and more  
104 expected to produce homogenous CCO nanopowders. In addition, it has already  
105 shown that these methods have a positive impact on semiconductor efficiency (Paul  
106 et al. 2015; Peymanfar and Ramezanalizadeh 2018).

107 Thus, the ceramic  $\text{CuCr}_2\text{O}_4$  has been synthesized by two different synthesis  
108 methods, using the sol-gel and co-precipitation methods. The obtained solid powders  
109 were characterized by different analyses, and the properties of the two obtained  
110 powders were explored and compared. The final aspect of this study was the  
111 examination and modeling of the photodegradation and the adsorption performances  
112 of CFC upon visible light irradiation using CCO as a semiconductor.

## 113 **2. Material and methods**

### 114 2.1 Chemicals

115 Copper nitrate trihydrate  $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$  (98% Fluka), chromium nitrate  
116 nonahydrate  $[\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$  (98% Biochem), Cefaclor Monohydrate  $\text{C}_{15}\text{H}_{14}\text{ClN}_3\text{O}_4\text{S}$   
117 and Polyvinylpyrrolidone (PVP) K30, procured from a pharmaceutical company  
118 Pharmalliance in Algeria, ethanol from Biochem, and NaOH, HCl, nitric acid from  
119 Sigma Aldrich, were utilized in the research. All used chemicals are of analytical  
120 grade.

### 121 2.2 Synthesis of $\text{CuCr}_2\text{O}_4$ via sol-gel method

122 CCO was synthesized via the aqueous PVP sol-gel method (Figure S.2 a). The  
123 gel was prepared using stoichiometric amounts (1:2 ratio) of copper nitrate trihydrate  
124  $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$  and chromium nitrate nonahydrate  $[\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$  respectively,  
125 which were dissolved in ethanol separately by using a magnetic stirrer, an excess of  
126 5% citric acid was added in the solutions. After a total solubility, the two solutions  
127 were mixed and were placed on a hot plate at 50 °C for 1h. Then,  
128 Polyvinylpyrrolidone (PVP K30) as a complexing agent (15% w/w (Giannopoulou et  
129 al. 2015)) was dissolved in 50 ml water and added dropwise to the reaction medium.  
130 Subsequently, to the concentration of the solutions by evaporation at 80 °C for 20 hrs

131 under stirring, the mixed solution turned into a black gel. The obtained gel was dried  
132 at 200 °C for 6 h and an auto combustion reaction took place giving a precursor  
133 powder (Xerogel).

134 The amorphous powder was ground and subjected to calcination at 700°C in an air  
135 atmosphere for 6 hours (Mobini et al. 2017). The synthesized sample was annealed  
136 to improve the degree of crystallinity as well as to eliminate any carbonaceous  
137 residue left after the combustion reaction. Then, the resulting nanopowder was  
138 subjected to phase identification, comparative and application studies.

### 139 2.3 Synthesis of $\text{CuCr}_2\text{O}_4$ via co-precipitation method

140 CCO was prepared by chemical co-precipitation (Figure S.2 b). Stoichiometric  
141 amounts 1:2 of copper nitrate trihydrate  $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$  and chromium nitrate  
142 nonahydrate  $[\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$  were totally dissolved in an aqueous solution, then 5%  
143 of concentrated  $\text{HNO}_3$  was added under continuous magnetic stirring.  $\text{NaOH}$  6 M  
144 solution was dropped into the bleu mixture with vigorous stirring to keep the pH in the  
145 range (9-10). A black to bluish precipitate was produced immediately confirming the  
146 formation of CCO spinel. Consequently, the precipitate was filtered and washed  
147 several times repeatedly with distilled water then dried at 120 °C for 24 h in an  
148 autoclave; then, the precursor powder was ground to a fine powder.

149 The obtained powder was annealed at 700°C under air for 6 hours to remove  
150 possible residual organic matter and to obtain a single crystalline phase (Mobini et al.  
151 2017). Moreover, the as-synthesized sample was subjected to phase identification,  
152 comparative and application studies.

### 153 2.4 Photocatalyst characterization

154 The phase analysis was investigated by X-ray diffractometer (XRD) in the range  
155 from 5 ° to 80 °. with Phillips PW 1730, X-ray diffractometer using monochromatized  
156 Cu K radiation ( $\lambda = 0.15417$  nm). The surface morphology of the sample SEM was  
157 observed by using Scanning Electron Microscope Brilliance 180P. as well as  
158 transmission electron microscope (TEM JEOL-24011BU) considered to take images  
159 of the nanostructures. ATR-FTIR spectra were achieved in the range of 400–4000  
160  $\text{cm}^{-1}$  by using an Alpha Bruker spectrometer. UV–visible diffuse reflectance spectrum  
161 (DRS) of the sample was measured with dry pressed disk samples through Cary  
162 5000 UV–vis equipped with the integration sphere.

## 163 2.5 Adsorption procedure

164 Cefaclor antibiotic (CFC) was chosen as a pharmaceutical contaminant model  
165 to investigate the adsorption performance of the two samples of CCO. The  
166 adsorption of CFC was conducted in batch mode by mixing 0.1 g of catalyst and  
167 solution CCF (100 mL) with an initial concentration of 10 mg/L. The solution was  
168 continuously stirred in the dark at a fixed ambient temperature in a closed reactor for  
169 2 hours. At a regular interval of time, 2 mL of sample was taken and separated by  
170 centrifugation at the speed of 5,000 rpm for 10 min. the aliquot concentration was  
171 directly analyzed by UV-Visible spectrometry (OPTIZEN, UV-3220UV) at the  
172 maximum absorption wavelength of CFC (264 nm) (Fig. S.3). It should be mentioned  
173 that the small positive error of UV-Visible spectrometry in comparison with HPLC was  
174 considered insignificant and hence ignored. The experiments were done in triplicate  
175 under the same conditions. The adsorption rate of CFC was calculated using the  
176 following equation (1):

$$177 \text{ Adsorption } (t)\% = \frac{(C_o - C(t))}{C_o} \times 100 \quad (1)$$

178 Where  $C_o$  ( $\text{mg.L}^{-1}$ ) is the initial concentration of CFC and  $C(t)$  ( $\text{mg.L}^{-1}$ ) is the  
179 concentration of CFC at a given time  $t$  (min).

## 179 2.6 Photocatalytic procedure

180 The photocatalytic degradation of CFC was conducted using 0.1g of CCO  
181 added to 100 mL of CFC solution with 20 mg/L initial concentration in a natural pH ~  
182 6, as those are the optimal conditions for the observation of the photodegradation  
183 process as 10 mg/L initial concentration of CFC was partially removed by adsorption.  
184 The suspension was continuously stirred for 120 min in dark condition in a closed  
185 reactor to reach the balance of adsorption and desorption before switch on the visible  
186 light. A tungsten lamp (200 W) was used as a visible light source. With a cooling  
187 system, the temperature of the solution during all the photocatalytic experiments was  
188 kept constant. Aliquot of 3 mL was withdrawn from the mixture at a predetermined  
189 time centrifuged before further analysis. The experiments were performed in triplicate  
190 under the same conditions for adsorption and photodegradation experiments. The  
191 photodegradation rate of CFC was calculated using the following equation (2):



$$\text{Photodegradation } (t)\% = \frac{(C_{Ad} - C(t))}{C_{Ad}} \times 100 \quad (2)$$

192 Where  $C_{ad}$  (mg/L) is the initial concentration of CFC after adsorption and  $C(t)$  (mg/L)  
193 is the concentration of CFC at time  $t$  (min).

## 194 2.7 Adsorption and photodegradation kinetics study

195 Adsorption Kinetics and mechanism study are essential in the treatment of  
196 aqueous wastewater as it provides valuable information on of adsorption process.  
197 Adsorption kinetics experimental data is generally presented by a pseudo-first- or  
198 pseudo-second-order law. Equation (3) represents a pseudo-first-order model of  
199 Lagergren (S Lagergren, S LAGERGREN, S.Y. Lagergren, SY Lagergren 1898) with  
200 a rate constant  $k_1$  ( $\text{min}^{-1}$ ) and  $q_e$  the maximum amount of CFC adsorbed at  
201 equilibrium. The plot of  $\ln(q_e - q_t)$  against  $t$  permit the determination of  $k_1$  and  $q_e$ ,  
202 respectively.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \cdot t \quad (3)$$

203 A pseudo-second-order law can be represented by equation (4), where  $k_2$  stands for  
204 the pseudo-second-order rate constant  $g$  ( $\text{mg} \cdot \text{min}^{-1}$ ) (Y.S. Ho 1998, 1999). Both  
205 parameters  $q_e$  and  $k_2$  can be obtained from the slope and intercept of  $t/q_t$  versus  $t$   
206 graph.

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (4)$$

207 The uptake and photodegradation of CFC can be controlled by either the mass  
208 transfer through the boundary film of liquid or by the intra-particle mass transfer.  
209 The linearized equation of mass transfer kinetic model proposed by Ketcha Mbadcam  
210 et al (Mbadcam et al. 2011), is expressed as follows:

$$\ln(C_0 - C_t) = \ln(D) + k_0 \cdot t \quad (5)$$

211 where  $C_0$  and  $C_t$  are respectively the initial concentration and concentration of solute  
212 ( $\text{mg} \cdot \text{L}^{-1}$ ) at an instant  $t$  (min),  $D$  is the mass transfer constant and  $k_0$  ( $\text{min}^{-1}$ ) the  
213 adsorption constant. CFC may be conveyed from the solution to the solid particles by  
214 the intra-particle diffusion/transport process. Sometimes, such a mechanism model is  
215 a rate-limiting step in the adsorption or photodegradation process. The probability of  
216 intra-particle diffusion is examined through the Weber and Morris diffusion model  
217 (El-Sikaily et al. 2007; Hameed et al. 2009):

$$q_t = k_{dif} \cdot t^{1/2} + C \quad (6)$$

218 where the intercept C provides information about the thickness of the boundary layer.  
 219 The intra-particle diffusion constant,  $k_{dif}$  values (in  $\text{mg.g}^{-1}.\text{min}^{1/2}$ ), for the tested  
 220 adsorbent are obtained from the slopes of the graphs (Figures 15 and 16) as  
 221 illustrated in Table 3 and 4. The validity of these models is thereafter discussed  
 222 based on the regression coefficient  $r^2$ .

223

### 224 3. Results and discussion

#### 225 3.1 CCO Characterization results

226 In order to investigate the single phase of CCO in the samples, X-ray diffraction  
 227 (XRD) patterns after calcination were elucidated in figure 1. In both methods, almost  
 228 the same single phase of CCO without impurity was formed. The phase of the CCO  
 229 could be indexed to the typical diffraction lines of the bulk, all the peaks were  
 230 assigned to the single-phase spinel of  $\text{CuCr}_2\text{O}_4$  in good accordance with the standard  
 231 card (JCPDS 98-005-9266) (Villars and Cenzual; Dollase and O'Neill 1997). The only  
 232 difference observed was the crystallite size which was calculated with the following  
 233 Debye-Scherrer formula Eq. (3) and which could be due to the high intensity of all  
 234 peaks. The crystalline size for the sol-gel method was found to be in the range of  
 235 17.45 to 26.24 nm and for co-precipitation, it was in the range of 20.97 to 36.86 nm.

$$D = \frac{K\lambda}{\beta \cos(\theta)} \quad (3)$$

236 where  $D$  is the average crystallite size of the phase under investigation in  
 237 nanometers,  $K$  is the Scherrer constant,  $\lambda$  is the wavelength of X-ray beam used,  $\beta$  is  
 238 the full width at half maxima (FWHM) in radians and  $\theta$  is the Braggs angle.

239 The X-ray density was estimated from the standard relation shown in equation (4)  
 240 (Kenfoud et al. 2020).

$$\rho = \frac{ZM}{N_A V} \quad (4)$$

241 Where  $N_A$  is Avogadro's number ( $6.02 \times 10^{23} \text{ mol}^{-1}$ ),  $M$  is the molecular weight of  
 242 CCO ( $231.535 \text{ g.mol}^{-1}$ ),  $Z$  is the number of formula unit present in a unit cell ( $Z = 4$ )

243 and  $V$  is the volume of the unit cell ( $283.05 \times 10^6 \text{ pm}^3$ ) The X-ray density for both  
244 methods was found to be  $5.43 \text{ g.cm}^{-3}$ .

245 Significant parameters including particle size, shape and density are associated with  
246 the specific surface area (SSA) measurements ( $\text{m}^2\cdot\text{g}^{-1}$ ). Using the Brunauer-Emmett-  
247 Teller (BET) equation (5) (Bykkam et al. 2015), the specific surface area of CCO  
248 nanoparticle was measured.

$$S = \frac{6 \times 10^3}{Dp \times \rho} \quad (5)$$

249 where  $Dp$  is the size of the particles,  $S$  is the specific surface area, and  $\rho$  is the X-ray  
250 density of CCO  $5.43 \text{ g.cm}^{-3}$ . Using this formula SSA was found to be 50.58 and 38.22  
251  $\text{m}^2\cdot\text{g}^{-1}$  for the nanoparticles obtained by the sol-gel and the co-precipitation methods,  
252 respectively. Consequently, very fine nanoparticles were obtained by the sol-gel  
253 method, the smaller the particle size of the catalyst, the bigger the particular surface  
254 area. A high catalyst surface area may result in better catalytic activity.

255 Fig. 1 XRD diffractogram of CCO (a) co-precipitation (b) sol-gel.

256 For the structural investigation of CCO, the XRD of the sol-gel was chosen and  
257 a Rietveld refinement method supplied by Maud software (version 2.93) was used.  
258 The experimental points are given as dot (.) and theoretical data determined by Maud  
259 are shown as a red line (Fig. 2). The difference between theoretical and experimental  
260 data is shown as the bottom line. The vertical lines reflect the approved Bragg's  
261 peaks. The results (Fig. 2) showed a strong matching with the findings calculated by  
262 the technique Rietveld and those observed in the experimental X-ray diffraction  
263 patterns.

264 The refined values represented an orthorhombic structure (space group  
265  $Fddd:2$ ) which is different from the database. In comparison with other known  
266 methods of structural properties, the Rietveld refinement results gave identical results  
267 (YE, Zuo-Guang; Dollase and O'Neill 1997). The refinement was done by calculating  
268 the reliability factors such as profile  $R_p$ , expected profile  $R_{exp}$ , and weighted profile  
269  $R_{wp}$  and Sig (GOF) which is the strength of the ratio of  $R_{wp}$  to  $R_{exp}$  (Akhtar et al.  
270 2019). For refined structural parameters, GOF must be close to 1. Rietveld refined  
271 parameters (R-factors) with the cell parameters (a,b,c) and atomic position (x,y,z) of  
272 Rietveld are described in Table 1. The inset in Figure 2 showed the schematic

273 representation of the CCO structure by Vesta (version 3.4.0) using the parameters of  
274 the table.

275 Fig. 2 Reitveld refined XRD diffractograms. Inset: the structural representation of CCO.

276 Table. 1 Rietveld refined parameters from MAUD software.

277 Phase crystallite of  $\text{CuCr}_2\text{O}_4$  can be confirmed by FTIR analysis and support  
278 the conclusion drawn by XRD data shown in Fig. 3. One can see that both methods  
279 showed the same FTIR spectrum with the absence of any vibration band attributable  
280 to carbonates. The synthesized CCO showed broad absorption bands arising from  
281 O–H stretching and bending vibration of water at  $3000\text{ cm}^{-1}$  (Geng et al. 2012). The  
282 same three strong absorption bands observed in both sol-gel and co-precipitation  
283 samples in the region of  $600\text{--}480\text{ cm}^{-1}$  belonged to the typical metal-oxygen (M–O)  
284 stretching vibrations (Geng et al. 2012; Mobini et al. 2017; Ramezanalizadeh et al.  
285 2019). The two peaks at  $599.79\text{ cm}^{-1}$  and  $552.35\text{ cm}^{-1}$  confirmed the formation of  
286 spinel copper chromite powder, which arose due to the stretching vibration of  $\text{Cr}^{3+}\text{--}$   
287  $\text{O}^{2-}$  at tetrahedral and octahedral sites coordination existence (Mobini et al. 2017).  
288 Also, the absorption peak at  $488.61\text{ cm}^{-1}$  corresponds to the metal-oxygen (Cu–O)  
289 vibration bond in the complex (Ramezanalizadeh et al. 2019). Moreover, the  
290 absorption bands appeared at  $552.35\text{ cm}^{-1}$ . could also be related to the stretching  
291 vibrations of the Cr–O–Cu structure (Mobini et al. 2017).

292 Fig. 3 Fourier transform infrared (FTIR) spectra of CCO.

293 In order to examine the morphology and structures of the prepared samples,  
294 Scanning Electron Micrograph (SEM) and transmission electron microscope (TEM)  
295 techniques were investigated. Figure 4 (a, b) shows typical SEM images of the sol-  
296 gel sample. The sample was made up of ultra-fine nanoparticles. These particles  
297 displayed some agglomerated morphology because of the nature of the sample.  
298 Also, the SEM images of the co-precipitation sample Figure 4 (c, d), show a high rate  
299 of porosity. The suspension viscosity plays a significant role in developing the porous  
300 structure. With the increase in the viscosity of the suspension, the porous structure  
301 becomes compact (Tripathy et al. 2016).

302 Fig. 4 SEM images of CCO (a, b) sol-gel (c, d) co-precipitation.

303 The CCO's sol-gel TEM images shown in figure 5 (a) gives clear information  
304 regarding the shape and size distribution of the sol-gel nanoparticles. As can be

305 seen, this sample was composed of approximately 25 nm particles on average, which  
306 agrees well with XRD results. However, for the co-precipitation sample, the particle  
307 sizes were estimated to be 40 nm (figure 5 c). It can be seen from the images that  
308 the sol-gel process produced smaller nanoparticles than the co-precipitation method.  
309 Moreover, the figures also clearly show that the particle aggregation led to  
310 aggregates of an average at the nanometers scale, which was higher for the sol-gel  
311 method. Furthermore, the lattice fringe in figures 5 (b and d) corresponded to [121]  
312 plane (orientation of the crystallites) of  $\text{CuCr}_2\text{O}_4$  spinel with a diffraction angle ( $2\theta$ ) of  
313 35.25 (Mohammad Kabir Hossain 2013). For the two preparation methods, the  
314 electron diffraction patterns of the samples were the same due to their structure  
315 which was confirmed by the XRD results.

316 *Fig. 5 TEM images of CCO (a, b) sol-gel (c, d) co-precipitation.*

317 Optical properties of CCO samples were measured using the UV–Vis diffuse  
318 reflectance spectrum. As shown in figure 6, the direct bandgap was estimated to be  
319  $0.92 \pm 0.1$  eV for co-precipitation, and  $0.94 \pm 0.1$  eV for the sol-gel method, mostly  
320 identical and close to the literature values (Lahmar et al. 2012; Akhundi and Habibi-  
321 Yangjeh 2017). The increase of gap energy value in the sol-gel method can be  
322 explained by the decrease of the particle size (Wang et al. 2015). Compared to  $\text{TiO}_2$   
323 and  $\text{ZnO}$  (Serpone 2006; Miki-yoshida 2016), both methods exhibited excellent  
324 absorption ability and can efficiently absorb visible light. Consequently, the rate of  
325 formation of electron-hole pairs on the surface of the photocatalyst also greatly  
326 increases under visible light irradiation.

327 *Fig. 6 UV–Vis diffuse reflectance spectrum (a) co-precipitation (b) sol-gel.*

### 328 3.2 Adsorption performance of CCO

329 A set of experiments were carried out by adding 0.1 g of each catalyst,  $\text{CCO}_{\text{sg}}$   
330 and  $\text{CCO}_{\text{cp}}$  nanoparticles, to 100 mL of CFC  $10 \text{ mg}\cdot\text{L}^{-1}$  with initial concentration at pH  
331 = 6 and for a contact time 120 min in darkness (lamp OFF).

332 Figure 10 depicts the impact of contact time on CFC adsorption onto  $\text{CCO}_{\text{sg}}$   
333 and  $\text{CCO}_{\text{cp}}$  nanopowders for two different initial concentrations at 298 K. It can be  
334 deduced that the adsorption of CFC varies proportionally with time achieving its  
335 optimum adsorption capacities  $q_e$  within 70 minutes regardless of the adsorbent and  
336 initial concentration value. Subsequently, the CFC adsorption remains unchangeable

337 with time increment. Therefore, 70 minutes can be considered the appropriate time to  
338 obtain equilibrium.

339 Fig. 7 Equilibrium time for adsorption of CFC (initial concentration:10 and 20 mg/L) on both  
340 nanomaterials.

341

342 The plots in Figure S4 of  $\ln (q_e - q_t)$  against  $t$ , display linearity with correlation  
343 coefficients  $r^2$  value, which are generally less than 0.9 in most cases. Besides, the  
344 calculated values of  $q_e$  are by far less than the obtained experimental values (Table  
345 2). Whereas, the pseudo-second-order model plot of  $t/q_t$  versus time, (Figure S5),  
346 shows a better fitting for the data ( $r^2 > 0.99$ ). Moreover,  $q_e$  values calculated from the  
347 linear plot of the pseudo-second-order kinetic equation are almost equal to those  
348 obtained from the experiments (Table 2). Consequently, it can be confirmed that the  
349 CFC adsorption onto  $\text{CCO}_{\text{SG}}$  and  $\text{CCO}_{\text{CP}}$  adsorbent obeys a pseudo-second-order  
350 reaction rate.

351 Table 2 kinetics models parameters for the adsorption of CFC by both nanomaterials.

352 The intra-particle diffusion kinetic model may govern the adsorption of CFC at  
353 the adsorbent surface. From Fig 8, it may be seen that there are two separate stage  
354 sorption, i.e., multi-linear in the case of  $\text{CCO}_{\text{CP}}$  adsorbent (Royer et al. 2009; Yazdani  
355 et al. 2016). The first straight portion, a sharp one, can be attributed to the transport  
356 of CFC across the bulk of the solution to the external surface of  $\text{CCO}_{\text{CP}}$  through the  
357 boundary layer, macropore diffusion (Allen et al. 1989). Meanwhile, the second linear  
358 portion may mention the final equilibrium where the intraparticle diffusion slowdown  
359 owing to the low concentration of CFC, meso- and micropore diffusion (Allen et al.  
360 1989). This leads to the suggestion that the adsorption can follow multiple-sorption-  
361 rates. The adsorption of CFC onto  $\text{CCO}_{\text{SG}}$  adsorbent displays only one straight line  
362 affirming that the intra-particle diffusion model is the rate-limiting in this case (Fig.S1).  
363 The intra-particle diffusion plots are shown in Figure 8, and the main parameters of  
364 this model are calculated and listed in Table 3. The values of intercept C provide  
365 information about the thickness of the boundary layer, i.e., the resistance to the  
366 external mass transfer. The larger values of the constants shown in Table 3 reflect  
367 more significant effects of the solution boundary layer (El-Sikaily et al. 2007; Hameed  
368 et al. 2009).

369 Fig. 8 Intra-particle diffusion plots for adsorption of CFC (initial concentration:10 and 20 mg/L) on both  
370 nanomaterials.  
371

372 Table 3 Intraparticle model parameters for the adsorption of CFC by both nanomaterials.

373 The adsorption efficiency of CFC differs. As can be shown in Figure 7,  
374 adsorption efficiency by  $\text{CCO}_{\text{cp}}$  and  $\text{CCO}_{\text{sg}}$  catalysts for an initial 10 mg/L  
375 concentration is 58 % and 52 %, respectively which shows clearly that  $\text{CCO}_{\text{cp}}$  has  
376 better adsorption. The same observation for 20 mg/L. The higher adsorption obtained  
377 with nanoparticles synthesized via co-precipitation method can be due to the porosity  
378 of the sample, in agreement with the SEM images (Figure 5 (c, d)). While The low  
379 adsorption in the  $\text{CCO}_{\text{sg}}$  sample was less important.

380 In addition, the advantage of high and rapid adsorption of CFC onto  $\text{CCO}_{\text{sg}}$  and  
381  $\text{CCO}_{\text{cp}}$  enhanced the interfacial interactions between CCF and surface catalysts. It is  
382 well known that more extrinsic adsorption leads to an increase the photodegradation  
383 activities.

### 384 3.3 Photocatalytic performance of CCO

385 The photocatalytic activity of  $\text{CCO}_{\text{sg}}$  and  $\text{CCO}_{\text{cp}}$  catalysts was evaluated  
386 through the CFC degradation with making ON the lamp. In addition, the test of CFC  
387 photolysis was evaluated in the absence of a catalyst using visible light irradiation  
388 under the same conditions. the obtained results of photodegradation in Figures 9 and  
389 10 demonstrate the difference between the catalysts and photolysis. As observed,  
390 photolysis led to a very low CFC degradation yield, lower than 5%; this can be  
391 explained by the low absorption of visible light (Fig S3). On the other hand, in the  
392 presence of photocatalyst, the degradation rate of CFC reached 57 % within 4 hours  
393 for the  $\text{CCO}_{\text{sg}}$ , while it was lower for the  $\text{CCO}_{\text{cp}}$  catalyst 49 %. This difference can be  
394 due to the ultrafine nature of the sol-gel nanoparticles, which gives a higher specific  
395 surface area as confirmed by the characterization.

396 Fig. 9 Equilibrium time for photodegradation of CFC (initial concentration: 20 mg/L) on both  
397 nanomaterials.

398 Fig. 10 Kinetic UV photocatalytic degradation of CFC with both nanomaterials  $\text{CCO}_{\text{SG}}$  and  $\text{CCO}_{\text{CP}}$ .

399

400 The kinetics results of photocatalytic degradation under visible irradiation are  
401 illustrated in Figures 9 and 10. According to the regression coefficient, mainly greater

402 than 0.98, the experimental results are well simulated by the Lagergren pseudo-first-  
403 order model for both tested adsorbents. The obtained apparent rate constants,  $k_{deg}$ ,  
404 and  $r^2$  values, obtained from the plot of  $C_t/C_0$  against  $t$ , are assembled in Table 4. As  
405 can be noted, in Fig. 10 photolysis does not affect the degradation of CFC, but the  
406 presence of the photocatalyst reduces extremely the concentration of CFC.

407 Table 4 Intraparticle and Lagergren pseudo-first-order model constants for the photodegradation of  
408 CFC by both nanomaterial SG and CP.

409 The photodegradation of CFC at the surface of the adsorbent may be  
410 governed by the intraparticle diffusion kinetic model, since,  $q_t$  and  $t^{1/2}$  convene a  
411 linear correlation (Fig. S6). Besides, the regression coefficient values are higher than  
412 0.96, denoting the relevance of the data in the model. The intra-particle diffusion  
413 plots show that the main parameters of this model are calculated and collected in  
414 Table 4. The thickness of the boundary layer is strongly correlated to the intercept  
415 values. The larger intercept of the graph ( $C$  value, Table 4) indicates a more  
416 significant boundary layer effect.

417 In Fig. S.6, trend lines are plotted and do not pass through the origin. This  
418 observation can be ascribed to some level of boundary layer control. Such behavior  
419 is an indication that the intra-particle diffusion is not the sole rate-controlling step, as  
420 other kinetic processes may influence the photodegradation rate. In other words, all  
421 of these operations are operating concurrently and cannot be neglected (Royer et al.  
422 2009; Yazdani et al. 2016).

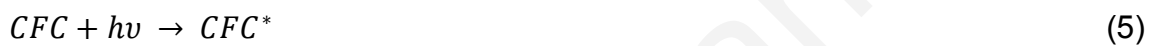
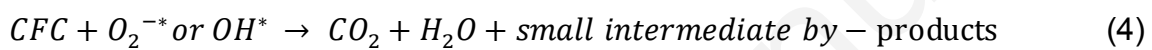
423 The mass transfer kinetic model constants are obtained from the slope and the  
424 intercept of the straight line of  $\ln(C_0 - C_t)$  versus time (Fig. S7 and S8). However, no  
425 linear relation was observed, and the regression coefficient is mainly very low and  
426 never exceeds 0.82. This result indicates that the uptake and photodegradation rate  
427 is not governed by mass transfer through a liquid film boundary, i.e., the convective  
428 mass transfer.

429 The photodegradation of organic compounds by a catalyst semi-conductor can  
430 be ascribed to different reaction pathways regulated by different active species such  
431 as  $\text{OH}^*$ ,  $\text{O}_2^*$ , and holes ( $h^+$ ) (Zuo et al. 2017). The energy band structure is a key  
432 factor that may affect the photocatalytic activity (Lahmar et al. 2017). UV-Vis was



433 used to analyze the optical properties of the catalysts and to deduce its forbidden  
434 bandwidth. CCO's clearly displayed a 0.9 eV bandgap energy (Fig. 9).

435 When photocatalytic reactions occur in an aqueous solution, the holes are  
436 effectively broken by water and generate hydroxyl radicals OH\*(Kumar et al. 2020). In  
437 our previous works (Belaissa et al. 2016; Abou Dalle et al. 2017; Aboudalle et al.  
438 2018; Zadi et al. 2018), it was proposed that both holes and hydroxyl radicals are  
439 involved as oxidizing agents responsible for CFC degradation. The basic process is  
440 illustrated in Fig. S9 and equations 1 to 5 suggest the following photodegradation  
441 mechanism under visible light irradiation:



442

#### 443 **4. Conclusion**

444 In the present work, CCO nanoparticles were successfully synthesized using  
445 co-precipitation and sol-gel methods. The catalysts were then characterized using  
446 several techniques to distinguish the effect of each synthesizing process. The XRD  
447 with Rietveld refinement, BET, SEM, and TEM confirmed that synthesized CCO via  
448 the sol-gel method has the smallest particle size. Moreover, its BET surface area was  
449 found to be higher than that achieved by the co-precipitation method, which suggests  
450 a higher photocatalysis activity. It should be noticed that the co-precipitation method  
451 gave a higher rate of porosity to the catalyst, leading to excellent adsorption property.  
452 Those characterizations were demonstrated using CFC as a target antibiotic example  
453 for testing the adsorption and photocatalytic performance of CCO.

454 The kinetics of the adsorption process was found to obey the pseudo-second-  
455 order law for both tested adsorbents. However, the Lagergren first-order model fits  
456 well with photodegradation experimental data. Whereas, the intra-particle diffusion  
457 model gave two distinct regions in the case of CFC adsorption by COC<sub>CP</sub>  
458 nanomaterial, i.e., a fast diffusion at the solution boundary film followed by slow intra-  
459 particle diffusion. The CFC adsorption occurs in one stage in the case of COC<sub>SG</sub>.

460 Similarly, the photodegradation process occurs in one step without passing through  
461 the origin, suggesting that the rate is not only controlled by the intra-particle diffusion  
462 process, particularly at its initial phase.

463 The adsorption and photocatalytic results showed that the catalyst synthesis  
464 method is a crucial parameter regarding the catalyst properties, such as particle size  
465 and morphology which can change the catalyst activity, as we noticed that SG has  
466 more photocatalytic activity. On the other hand, CP has a higher adsorption activity.  
467 Furthermore, this study showed that the CCO spinel might be an effective candidate  
468 for the treatment of other organic pollutants present in wastewater.

#### 469 **Declaration**

470

#### 471 **Ethics approval and consent to participate**

472 Not applicable

473

#### 474 **Consent for publication**

475 Not applicable

476

#### 477 **Competing interest**

478 The authors declare that they have no conflict of interest.

479

#### 480 **Authors contributions**

481 *Oussama Baaloudj and Mohamed Kebir*: investigation, formal analysis, visualization,  
482 writing original draft.

483 *Noureddine Nasrallah and Aymen Amin Assadi*: conceptualization, funding  
484 acquisition, methodology, resources, project administration, supervision, writing-  
485 review and editing.

486 *Loffi Khezami*: writing-review and experiment modeling and simulation

487 *Abdeltif Amrane*: investigation, visualization.

488

#### 489 **Availability of data and materials:**

490 The datasets used and/or analysed during the current study are available from the  
491 corresponding author on reasonable request.

492

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500

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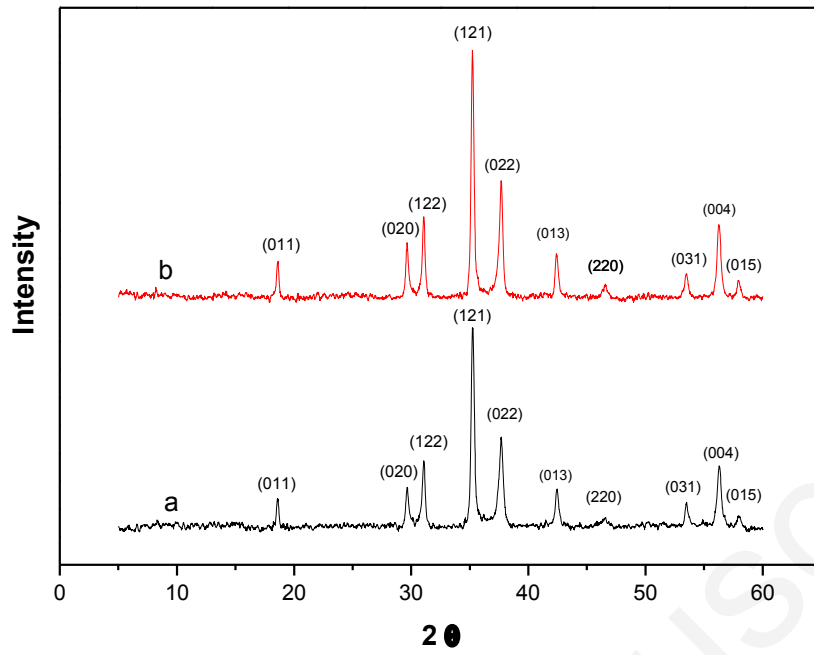


Fig. 1 XRD diffractogram of CCO (a) co-precipitation (b) sol-gel.

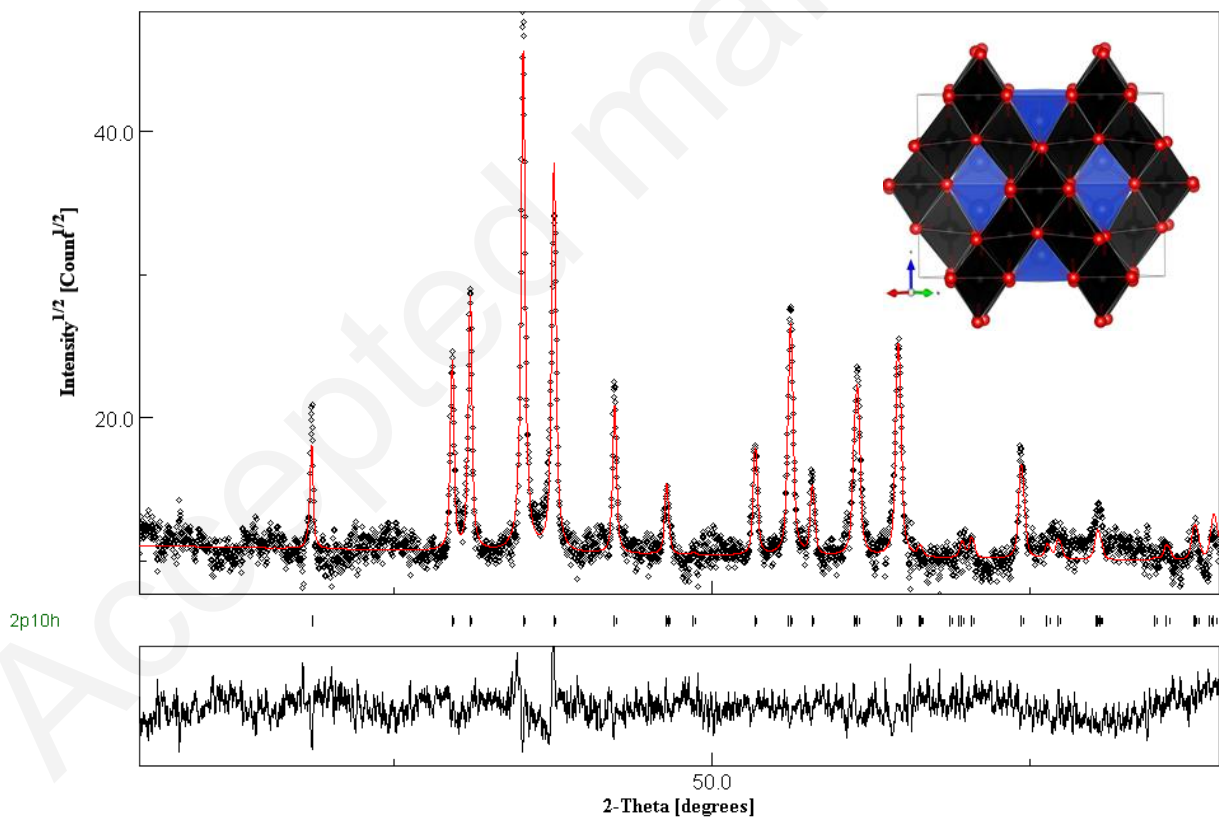
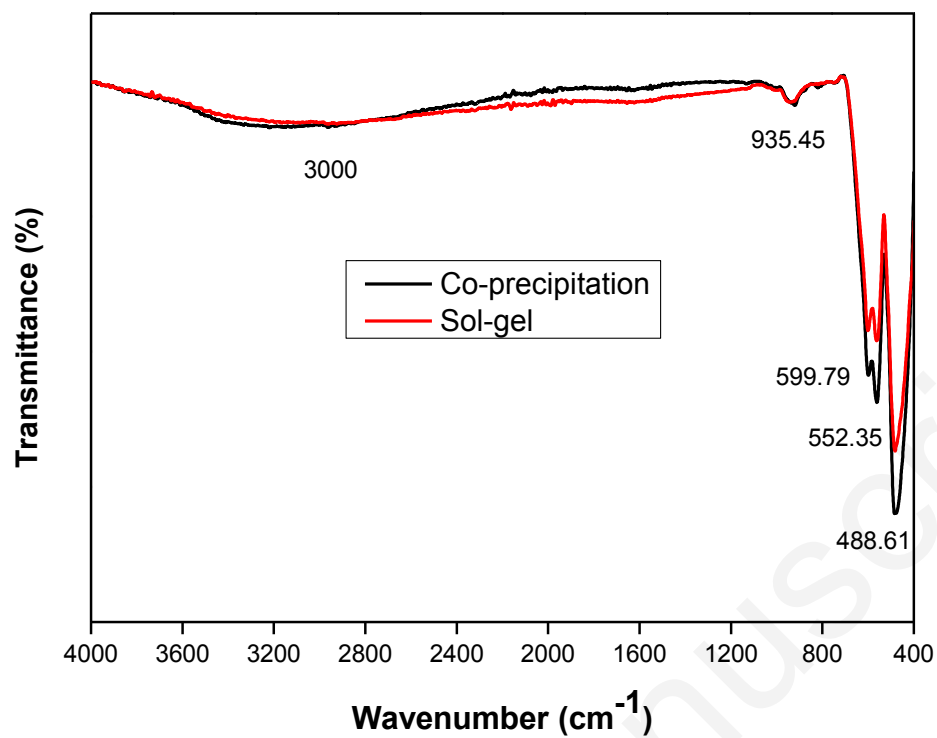
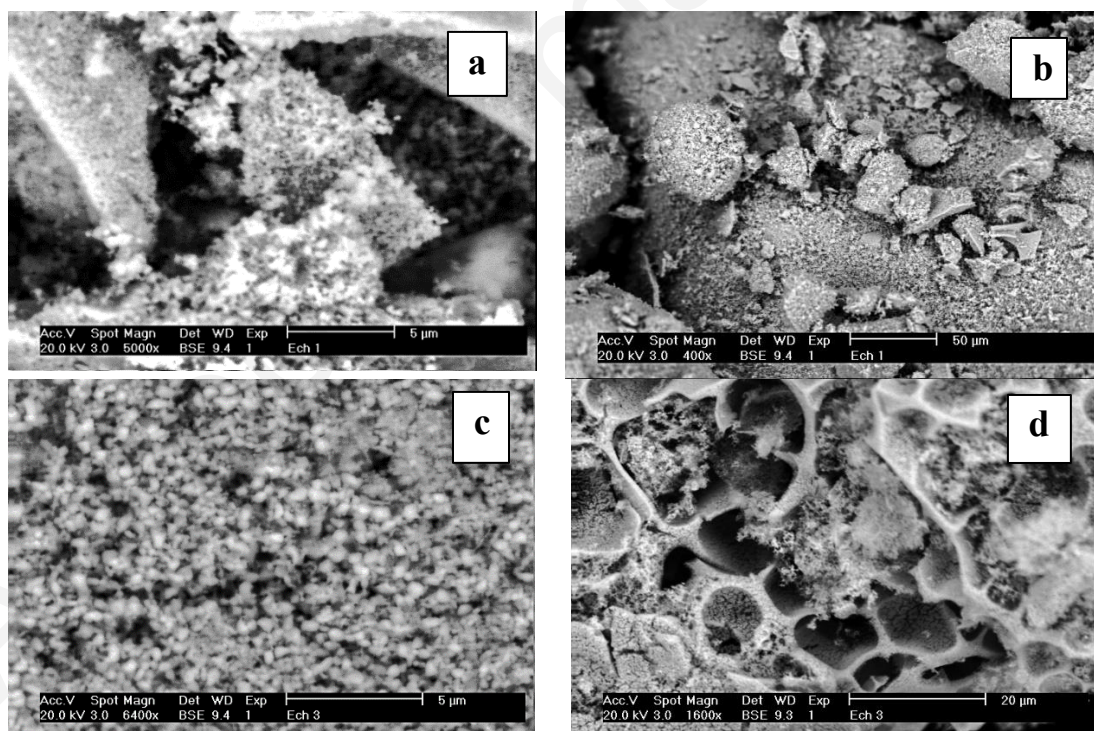


Fig. 2 Rietveld refined XRD diffractogram. Inset: the structural representation of CCO.



**Fig. 3** Fourier transform infrared (FTIR) spectra of CCO.



**Fig. 4** SEM images of CCO (a,b) sol-gel (c,d) co-precipitation.

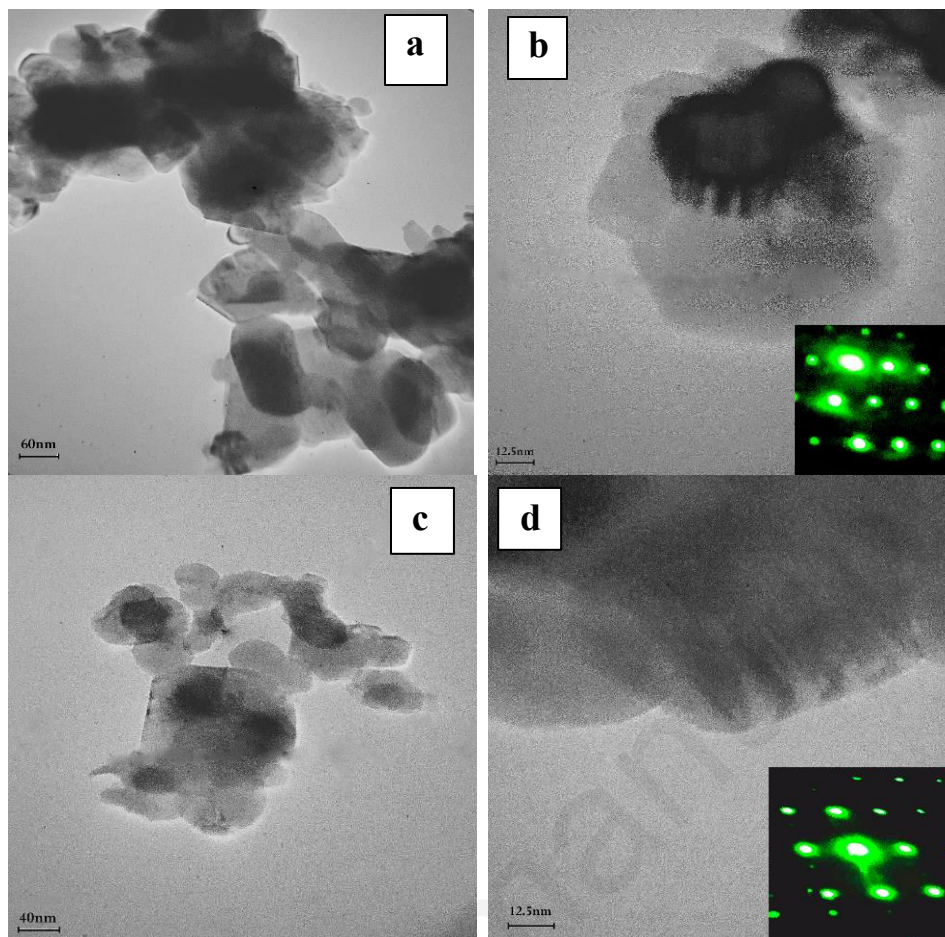


Fig. 5 TEM images of CCO (a,b) sol-gel (c,d) co-precipitation.

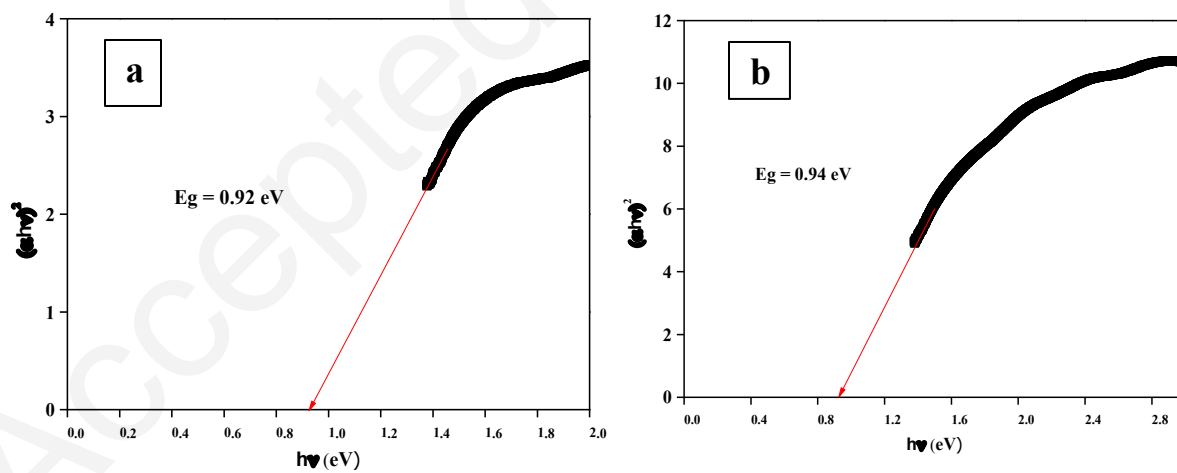
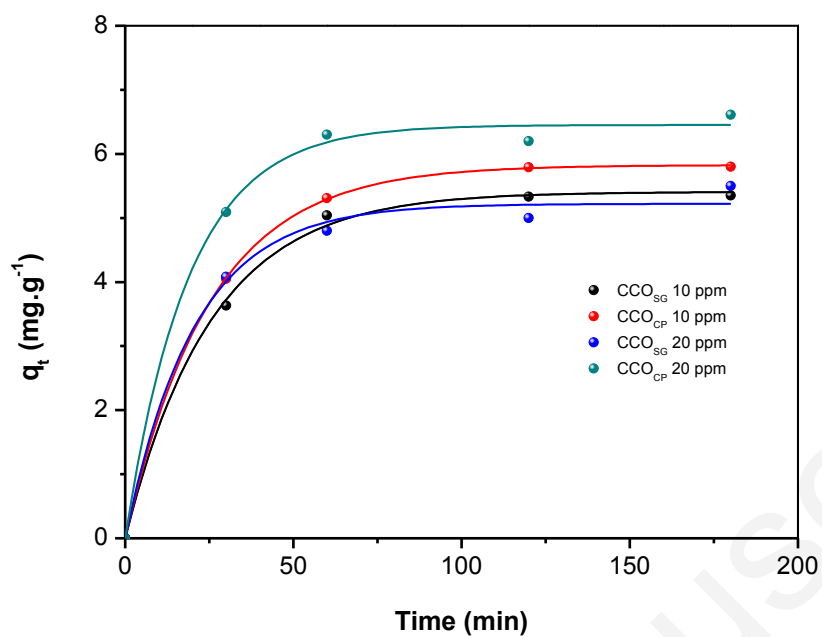
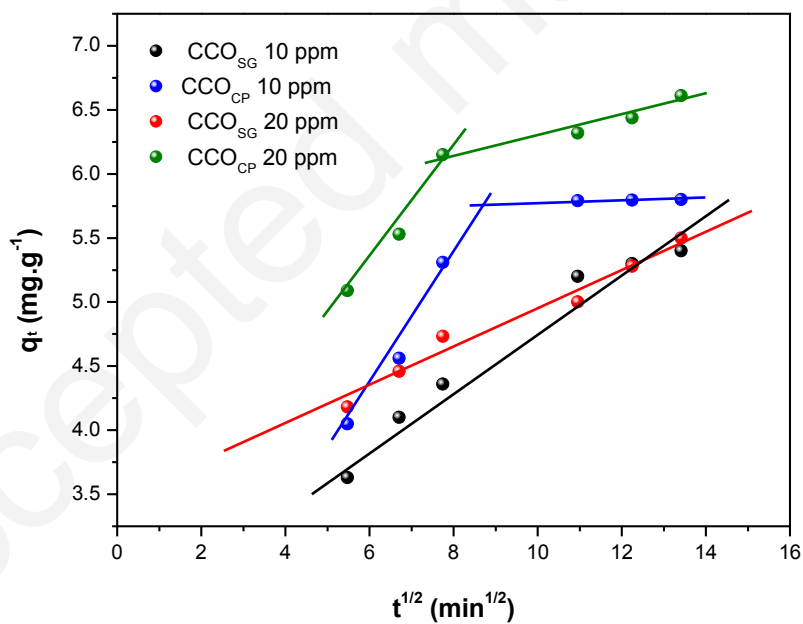


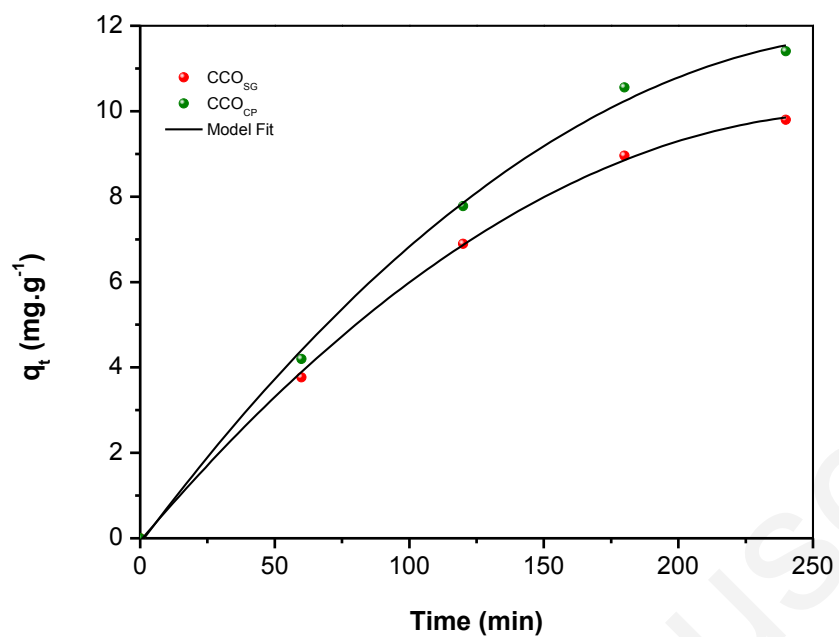
Fig. 6 UV-Vis diffuse reflectance spectrum (a) co-precipitation (b) sol-gel.



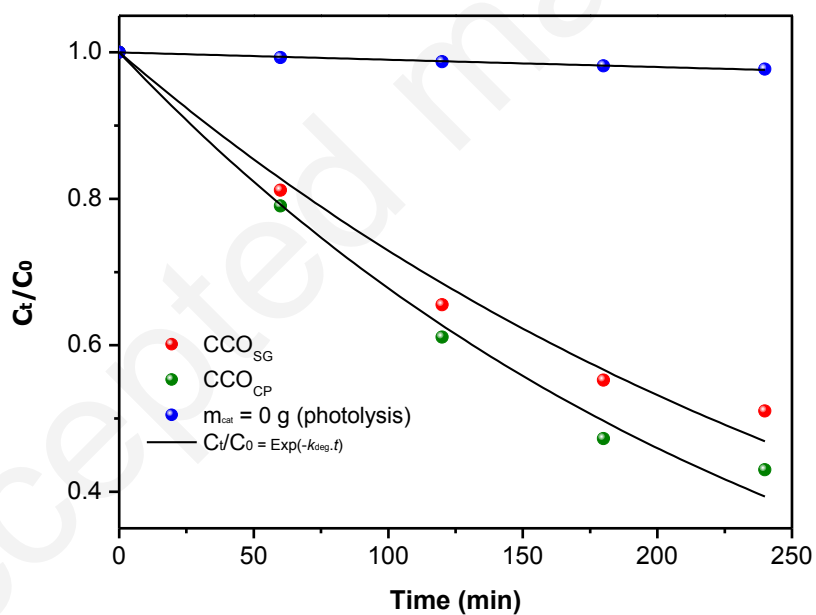
**Fig. 7** Equilibrium time for adsorption of CFC (initial concentration:10 and 20 mg/L) on both nanomaterials.



**Fig. 8** Intra-particle diffusion plots for adsorption of CFC (initial concentration:10 and 20 mg/L) on both nanomaterials.



**Fig. 9** Equilibrium time for photodegradation of CFC (initial concentration: 20 mg/L) on both nanomaterials.



**Fig. 10** Kinetic UV photocatalytic degradation of CFC with both nanomaterials CCO<sub>SG</sub> and CCO<sub>CP</sub>.