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Oussama Baaloudj, Nouredine Nasrallah, Mohamed Kebir, Bouzid Guedioura, Abdeltif Amrane, et al.. Artificial neural network modeling of cefixime photodegradation by synthesized CoBi(2)O(4) nanoparticles. *Environmental Science and Pollution Research*, 2021, 28 (12), pp.15436-15452. 10.1007/s11356-020-11716-w . hal-03037964

HAL Id: hal-03037964

<https://hal.science/hal-03037964v1>

Submitted on 19 May 2021

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1 **Artificial neural network modeling of Cefixime photodegradation by**
2 **synthesized CoBi₂O₄ nanoparticles**

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19

20 **Abstract**

21 CoBi₂O₄ (CBO) nanoparticles were synthesized by sol-gel method using
22 Polyvinylpyrrolidone (PVP) as a complexing reagent. For a single-phase with the spinel
23 structure, the formed gel was dried and calcined at four temperatures stages. Various
24 methods were used to identified and characterized the obtained spinel, such as X-ray
25 diffraction (XRD), Scanning Electron Micrograph (SEM-EDX), Transmission electron
26 microscope (TEM), Fourier transform infrared (FT-IR), X-ray fluorescence (XRF),
27 Raman and UV-Vis spectroscopies. The photocatalytic activity of CBO was examined
28 for the degradation of a pharmaceutical product Cefixime (CFX). Furthermore, for the
29 prediction of the CFX degradation rate an artificial neural network model was used.
30 The network was trained using the experimental data obtained at different pH with
31 different CBO doses and initial CFX concentrations. To optimize the network, various
32 algorithms and transfer functions for the hidden layer were tested. By calculating the

33 mean square error (MSE), 13 neurons were found to be the optimal number of neurons
34 and produced the highest coefficient of correlation R^2 of 99.6 %. The relative
35 significance of the input variables was calculated and the most impacting input was
36 proved to be the initial CFX concentration. The effects of some scavenging agents
37 were also studied. The results confirmed the dominant role of hydroxyl radical OH^\bullet in
38 the degradation process. With the novel $\text{CoBi}_2\text{O}_4/\text{ZnO}$ hetero-system, the
39 photocatalytic performance has been enhanced, giving an 80% degradation yield of
40 CFX (10 mg/L) at neutral pH in only 3 hours.

41 **Keywords:** CoBi_2O_4 Spinel, Characterization, Cefixime, Artificial neural network,
42 Optimization.

43 1. Introduction

44 In recent years, pharmaceutical compounds have sullied the aqueous environment,
45 among those compounds, antibiotics are the major concern which are extremely
46 dangerous because they are widely used in both human and veterinary medicines
47 (Kaczala and E. Blum 2015). Antibiotics are also used to improve feed quality and thus
48 increase rates in the poultry industries (World Health Organisation 2011). Analytical
49 study of antibiotic use in 76 countries from 2010-2015 found that global antibiotic
50 consumption has increased by 65% for the fifteen years studied (Sample 2018). The
51 majority of antibiotic products are not biodegradable and their environmental
52 contamination can increase aquatic toxicity (Mostafaloo et al. 2019). Generally,
53 antibiotics are present at amounts ranging from ng/L to $\mu\text{g/L}$ in treated wastewater
54 (Ibáñez et al. 2017; Shokoohi et al. 2017; Mirzaei et al. 2018). But even in small
55 amounts, the presence of these compounds in water supplies will increase bacterial
56 resistance, which produces a kind of micro-organisms called superbugs or antibiotic
57 resistance (ABR) that are considered to cause very dangerous health effects (Elder et
58 al. 2020). ABR is the ability to survive and multiply in the presence of antibiotic doses
59 that are eventually deemed effective against a bacterial population or other
60 microorganisms (Elder et al. 2020). A statistics study indicates that antibiotic resistance
61 causes 700,000 deaths globally each year (Liu et al. 2019). ABR is now, in the 21st
62 century, widely recognized as a grave threat to global health ~~in the 21st century~~
63 (Littmann et al. 2015).

64 As a typical example of antibiotics, Cefixime (CFX) was chosen which belonging to
65 broad-spectrum, third-generation cephalosporin antibiotic derived semi-synthetically
66 from the marine fungus *Cephalosporium acremonium* (Shooshtari and Ghazi 2017).
67 CFX with molecular formula $C_{16}H_{15}N_5O_7S_2$ (Fig. 1) is (6R,7R)-7-[[[(2Z)-2-(2-amino -1,3-
68 thiazol -4- yl) -2- (carboxymethoxyimino) acetyl] amino] -3- ethenyl -8- oxo -5- thia -1-
69 azabicyclo [4.2.0] oct-2-ene-2-carboxylic acid (Sheydaei et al. 2018). A study detected
70 CFX as one of the most prevalent antibiotics observed in different water environments
71 with concentrations of 278.65 to 422.1 ng/L (Mirzaei et al. 2018).

72 *Fig. 1 Molecular structure of the antibiotic Cefixime.*

73 Most of the conventional approaches that are commonly used for the removal of
74 antibiotics have no positive findings for the degradation of antibiotic residues from
75 contaminated waters or have substantial inconveniences such as by-products of the
76 degradation (Xiong et al. 2018; Zhu et al. 2018; Zhang et al. 2020). On the other hand,
77 Advanced Oxidation Processes (AOPs) have proven to be an effective solution for the
78 rapid degradation of non-biodegradable substances in polluted water (Lou et al. 2017;
79 Aboudalle et al. 2018; Kamagate et al. 2018). Particularly, the Heterogeneous
80 photocatalysis process which is one of the best approaches for aqueous environment
81 treatment as it is safer and a natural technology (used green energy). photocatalysis
82 has proven on a previous investigations a successful degradation for various types of
83 pharmaceutical drugs and organic compounds in the wastewater (Kamagate et al.
84 2018; Nguyen et al. 2018; Li et al. 2019b; Sayadi et al. 2019). Photocatalysis is based
85 generally on the principle of the activation of a catalyst using an energy provided by a
86 source of light (Homem and Santos 2011). As a catalyst, semiconductors are
87 commonly used as they are very effective and easy to synthesize. Recently, many
88 bismuth-based semiconductors have become very significant because of their high
89 chemical stability, their excellent ability to absorb light and its narrow optical band gap
90 (Tho et al. 2020). Cobalt bismuthate with the chemicals formula $CoBi_2O_4$ (CBO) was
91 chosen as a typical semiconductor. To our knowledge, only one study has dealt with
92 the synthesis and use of CBO photocatalyst (Jagadeesh and Sailaja 2019). Moreover,
93 no study has been made yet concerning $CoBi_2O_4/ZnO$ hetero-system.

94 Artificial neural network (ANN) is one of the most powerful tools for modeling linear
95 and non-linear systems (Mohammadzadeh Kakhki et al. 2020). It an effective way of
96 predicting experimental patterns in various systems, especially for photocatalysis

97 (Zhou et al. 2020) Moreover, ANN has the self-learning ability and to work with
98 incomplete knowledge, storing information on the entire network, having fault tolerance
99 and a distributed memory (Kaur and Kaur 2014). Thus, modeling and optimization can
100 be accomplished without the rigor of the experimental information via ANN (Ayodele et
101 al. 2020). Owing to that, ANN has been employed in the prediction of photocatalysis
102 CFX efficiency. The challenge in the ANN modeling is to build a network with the
103 smallest possible number of random experimental points to modulate and achieve the
104 expected results approach to real cases without designing an experimental model.
105 Only a few studies have attempted this challenge (Hassani et al. 2015; Tabatabai-
106 Yazdi et al. 2019; Zulfiqar et al. 2019). To find the most efficient and effective network,
107 various algorithms and transfer functions for the hidden layer has been attempted.

108 In this study, we report the synthesis of CoBi_2O_4 nanoparticles which prepared by
109 sol-gel auto combustion method using polyvinylpyrrolidone (PVP) as a complexing
110 reagent. Various methods were used to identified and characterized the obtained
111 spinel, such as XRD, SEM-EDX, TEM, FT-IR, XRF, Raman and UV-Vis
112 spectroscopies. After that, Cefixime was considered as a model of antibiotic compound
113 to tested the photocatalytic performance of this catalyst. The effect of pH, irradiation
114 time, the concentration of CFX and concentration of catalyst on the degradation of CFX
115 was examined and modeled using ANN. Also, a Garson formula was introduced to
116 measure the relative significance of different input variables. After that, the effects of
117 some scavenging agents have been studied. Finally, the new hetero-system
118 $\text{CoBi}_2\text{O}_4/\text{ZnO}$ has been tested in order to enhance the photocatalytic performance.

119 **2. Material and methods**

120 **2.1 Chemicals**

121 Chemicals used in the present study were bismuth nitrate pentahydrate
122 $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ (98.5% Chem-Lab), cobalt nitrate hexahydrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ (98%
123 Biochem), Zinc nitrate hexahydrate $[\text{N}_2\text{O}_6\text{Zn} \cdot 6\text{H}_2\text{O}]$ (98% Biochem), Cefixime
124 trihydrate and Polyvinylpyrrolidone were obtained from a pharmaceutical company
125 Pharmalliance Algeria, ethanol from Biochem, Sodium hydroxide, Hydrochloric acid,
126 isopropanol and nitric acid were supplied by Sigma Aldrich. All chemicals were used
127 as received without further purification. Distilled water has been used as a solvent.

128 2.2 Synthesis of CoBi₂O₄ nanoparticles

129 CoBi₂O₄ was synthesized by the aqueous PVP sol-gel method. The gel was
130 prepared using stoichiometric amounts (1:2 ratio) of cobalt nitrate hexahydrate
131 [Co(NO₃)₂·6H₂O] and bismuth nitrate pentahydrate [Bi(NO₃)₃·5H₂O] respectively. They
132 were then dissolved in ethanol by using a magnetic stirrer; an excess of 5% citric acid
133 was added in the solutions. After total solubilization, both solutions had been mixed
134 and heated at 50 °C for 1h.

135 In the following step, Polyvinylpyrrolidone (PVP K30), used as a complexing
136 agent was dissolved in 50 mL water and added to the reaction solution, applied about
137 15% w/w to obtain the complexing role (Giannopoulou et al. 2015). After concentrating
138 the solutions by evaporation at 80 °C under stirring, the mixed solution turned into a
139 reddish transparent gel. After drying and combustion at 200 °C for 6 h a precursor gel
140 powder was formed (Xerogel).

141 The amorphous powder was subjected to calcination at 300°C, 400°C, 600°C and
142 800°C in an air oven each one for 3 h. The synthesized sample was annealed to
143 improve the degree of crystallinity and to eliminate any leftover carbonated waste after
144 the combustion reaction. Then, it was subjected to phase identification, microstructural
145 analysis and photocatalytic studies.

146 2.3 Characterization

147 The XRD analysis of the products was recorded by a Phillips PW 1730, X-ray
148 diffractometer using monochromatized Cu K radiation ($\lambda = 0.15417$ nm the morphology
149 of the sample SEM was studied using the electron scanning microscope FEI Quanta
150 650 equipped with EDX and Mapping analysis with 20 kV accelerated voltage.
151 Transmission electron microscope (TEM) images of the nanostructures were taken on
152 a JEOL-24011BU. ATR-FTIR spectra were obtained in the range of 400–4000 cm⁻¹
153 with an Alpha Bruker spectrometer (One FTIR model). The chemical analysis was
154 carried out by using Xray fluorescence (PANalytical epsilon3-XL spectrometer). UV–
155 visible diffuse reflectance spectrum (DRS) of the sample was produced by dry pressed
156 disk sample using Cary 5000 UV–vis. The Raman analysis was carried out using
157 LabRAM HR Evolution system Horiba Jobin-Yvon.

158 2.4 Photocatalytic degradation study

159 We selected (CFX) as a pharmaceutical model contaminant to investigate
160 CoBi₂O₄'s photocatalytic performance. The photocatalytic degradation of CFX was
161 conducted by mixing an appropriate quantity of CoBi₂O₄ in 100 mL of CFX solution
162 with known concentration. The pH was set to the desired value with NaOH and HCl.
163 The solution was continuously stirred for 2h in dark conditions in a closed reactor to
164 reach the balance of adsorption and desorption before switching on the light. As a
165 visible light source, a tungsten bulb 200 W manufactured by Osram was applied and
166 positioned at 10 cm from the solution surface. The intensity (8.25 mW/cm²) and the
167 maximum emission (630 nm) of the lamp were measured by a digital flux meter (Testo
168 545). A cooling system consisting of a double-walled reactor attached to a thermostatic
169 bath (Daihan Labtech, LCB-11D) has been used to maintain the temperature of the
170 solution nearly constant (25 ± 1 °C) during the photocatalytic experiments. At a regular
171 time, 2 mL of the solution was centrifuged at the speed of 5,000 rpm for 10 min to filter
172 the suspended CoBi₂O₄ particles from the sample and directly analyzed by UV-Visible
173 spectrometry (OPTIZEN, UV-3220UV) at the maximum absorption wavelength of CFX
174 (288 nm). It should be mentioned that the small positive error of UV-Visible
175 spectrometry in comparison with HPLC was ignored. The following equation was used
176 to calculate the degradation rate of CFX.

$$Photodegradation\% = \frac{(C_o - C)}{C_o} \times 100 \quad (1)$$

177 Where C_o is the initial concentration of CFX after adsorption and C is the
178 concentration of CFX at time t.

179 As already mentioned, the CFX concentration was monitored by measuring the
180 absorbance of the samples using a UV–Visible spectrophotometry. The degradation of
181 the pollutant was followed by the disappearance of the band corresponding to CFX at
182 288 nm as shown in figure 2. The experiment was conducted in the presence of 0.1 g
183 CBO at pH 6, room temperature and an initial CFX concentration of 10 mg/L.

184 To evaluate the CFX mineralization by the catalyst CBO, the amount of total
185 organic carbon (TOC) in the solution at a regular time with the same conditions was
186 measured by TOC analyzer (Shimadzu TOC-L, Japan) using the catalytic combustion

187 method at 680°C. The results of TOC analysis are presented in Fig. 2 (b). The following
188 equation was used to calculate the TOC removal (%):

$$TOC_{removal}\% = \frac{(TOC_o - TOC)}{TOC_o} \times 100 \quad (2)$$

189 where TOC_o (mg) is the initial TOC values after adsorption, TOC (mg) is the remaining
190 TOC in solution.

191 the TOC removal reached 67.23% in the presence of CBO catalyst after 6 h, which
192 confirmed that cefixime could be effectively mineralized in the presence of CBO
193 photocatalyst under visible light irradiation.

194 *Fig. 2 (a) UV-visible spectra (B)TOC removal of CFX (10 mg/L).*

195 2.5 Experimental design and modeling

196 The input layer consisted of four numbers of neurons, which are pH, irradiation
197 time (min), the dose of CBO (g/L) and concentration of CFX (mg/L), while
198 photodegradation of CFX (%) was selected as the output layer. The application was
199 performed in the laboratory to obtain the actual responses. As it is a challenge to build
200 a network with the smallest possible number of random experimental points to
201 approach to real cases without designing an experimental model. For that, a total of
202 40 random experimental points has been randomly divided into 70% training, 15%
203 testing and 15% validation data. Training data were presented to the network during
204 training. The use of validation data was to test network generalization and to stop
205 training if generalization stops. The test data provided a fully independent network
206 performance measurement during and following training (Ayoubi-Feiz et al. 2019).

207 The modeling of the photodegradation of CFX was carried out by MATLAB
208 R2014a which has been widely used (Medarević et al. 2016; Ayoubi-Feiz et al. 2019;
209 Tabatabai-Yazdi et al. 2019; Zulfiqar et al. 2019; Garg et al. 2020). The model
210 parameters are described in Table 1. For the model development, the feed-forward
211 neural network with backpropagation method was used. Furthermore, a supervised
212 learning technique called Levenberg-Marquardt with a training function 'trainlim' has
213 been used for training the network.

214 *Table 1 ANN model parameters.*

215 The number of hidden neurons is a critical element of modeling experimental
 216 processes with ANN (Hazrati et al. 2017). For its optimization, a set of topologies have
 217 been used in which the number of hidden neurons changed from 2 to 20. The mean
 218 square error MSE was performed to investigate the relation between the hidden
 219 neurons and the network error (Ayoubi-Feiz et al. 2019). The MSE function was used
 220 as Eq.3. The coefficient of correlation R (Eq.4) used to predict model conformity and
 221 applicability, the more the value is close to one, the better it is applied.

$$MSE = \frac{1}{n} \sum_{i=1}^n (y_{i,NN} - y_{i,exp})^2 \quad (3)$$

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_{i,NN} - y_{i,exp})^2}{\sum_{i=1}^n (y_m - y_{i,exp})^2} \quad (4)$$

222 where n is the total number of data points, $y_{i,NN}$ and $y_{i,exp}$ are the network prediction
 223 and the experimental response and i is an index of the data, y_m is the average of the
 224 actual values.

225 3. Results and discussion

226 3.1 Characterization of the catalyst

227 To confirm the single phase of CoBi_2O_4 , an X-ray diffraction (XRD) pattern after
 228 each calcination was taken. Figure 3 illustrates the effect of different annealing
 229 temperatures on the structure of the synthesized samples. The pure CoBi_2O_4 nano-
 230 powders were obtained at 800 °C (after annealing at 300 °C, 400 °C, 600 °C) almost
 231 a single phase of CBO without impurity was observed. The phase of the CoBi_2O_4 could
 232 be indexed with the five main diffraction peaks at $2\theta = 27.88^\circ$ (111), 33.12° (200),
 233 45.72° (220), 52.76° (311) and 56.04° (222) which were in good agreement with the
 234 reference peaks (Jagadeesh and Sailaja 2019) almost the same, and also in line with
 235 the standard card (JCPDS 50-0369) from Joint Committee of Powder Diffraction
 236 Standards of the face-centered cubic of CoBi_2O_4 .

237 The crystallite size was calculated from the main diffraction peaks of the last
 238 calcined product (at 800 °C) with the following Debye- Scherer formula Eq. (5). The
 239 crystalline sizes have been estimated between 19.45 and 46.39 nm.

$$D = \frac{K\lambda}{\beta \cos(\theta)} \quad (5)$$

240 where D is the crystallite size of the phase-in nanometers, K is the Scherrer constant.
241 ($K = 0.94$ for cubic symmetry), λ is the wavelength of the X-ray beam used, β is the full
242 width at half maxima (FWHM) in radians and θ is the Braggs angle.

243 *Fig. 3 XRD diffractogram of CoBi_2O_4 calcined at (a) 300°C, (b) 400°C, (c) 600°C and*
244 *(d) 800°C.*

245 For the XRD patterns of the ZnO nanoparticles prepared via co-precipitation. As
246 shown in Figure 4, the ZnO nanoparticles displayed a Wurtzite structure (hexagonal
247 phase, space group P63mc). All standard peaks observed for ZnO nanoparticles were
248 in line with those obtained from (JCPDS 36-1451) (Raou 2017).

249 *Fig. 4 XRD diffractogram of ZnO.*

250 The spinel structure may be considered as a continuously bound crystal in which
251 the atoms are bonded by equivalent forces (ionic, covalent or van der Waals) to all
252 nearest neighbors. The spinel shaped metal ions are found in two separate sub-lattices
253 known as A-site (tetrahedral) and B-site (octahedral), as stated in the geometric
254 arrangement of the nearest oxygen neighbors (Sabri et al. 2016). Fourier transform
255 infrared spectra of CoBi_2O_4 recorded within the range of 4000–400 cm^{-1} are shown in
256 Figure 5. It is evident in the IR spectrum that CBO had five intensive absorption peaks
257 in the region of 400-900 cm^{-1} , which could be related to the typical metal-oxygen (M–
258 O) vibrations (Jasaitis et al. 2011). The presence of peaks between 570 cm^{-1} and 669.9
259 cm^{-1} belonged to the vibration of the Bi–O bond and the vibration peak at 824.28 cm^{-1}
260 can be assigned to Bi–O–Bi (Yang et al. 2018; Viruthagiri and Kannan 2019).
261 Furthermore, the appearance of Peaks 446.13 cm^{-1} and 532.31 cm^{-1} can probably be
262 related to the tetrahedral (CoO_4) in the spinel (Sousa et al. 2019).

263 *Fig. 5 FTIR spectra of CoBi_2O_4 .*

264 Figure 6 shows the Raman spectra of CoBi_2O_4 . There are five Raman-activated
265 bands; all these modes were observed at ambient conditions. The bands above 600
266 cm^{-1} were due to the motion of oxygen in the tetrahedral AO_4 octahedral BO_6 groups
267 (Li et al. 2019a), suggesting a certain amount of Co and Bi disturbance in the
268 tetrahedral and octahedral sites. The low-frequency modes observed at 54.13, 80.5
269 and 123.73 cm^{-1} can be related to the Bi^{3+} ion motion in the spinel layer and the mode
270 at 521.03 cm^{-1} can be attributed to the variation of bond distances between Bi atoms

271 and the spinel block apical O atoms (Zhang et al. 2018). The strongest band observed
272 at 264 cm^{-1} corresponded to O–Bi–O vibration (Zhang and Saxena 2013). The Raman
273 modes of 193.29 , 476.05 , 600 and 670 cm^{-1} were related to the vibration of the Co
274 atoms (Diallo et al. 2015). Besides, a small Raman band was observed at 151.35 cm^{-1} ;
275 the origin of this band is still unknown.

276 *Fig. 6 Raman spectra of CoBi_2O_4 .*

277 The morphology and structures of the prepared sample were visualized by
278 Scanning Electron Micrograph (SEM) and transmission electron microscope (TEM)
279 techniques were used. Figure 7 (a) shows a typical SEM image of the sample. It can
280 be observed that the sample consisted of particles exhibiting cubic morphology. Due
281 to the ultrafine nature of the sample, these particles displayed a slightly agglomerated
282 morphology. The TEM images of CoBi_2O_4 shown in figure 7 (b) demonstrate clear
283 information regarding the size, shape and size distribution of nanoparticles. Based on
284 the size distribution histogram in the inset figure, the catalyst was composed of particle
285 size in the range of 22 nm. It was found that the size of the crystallite obtained from
286 XRD analysis and the particle size obtained from TEM analysis were in the same size
287 order. This picture also shows the existence of several aggregations within the range
288 of nanometres.

289 The electron diffraction pattern of the nanoparticles are shown in figure 7 c, This
290 pattern has a cubic shape and right angles ($K/H = 1$, $(\vec{H}, \vec{K}) = 90^\circ$) which is defined as
291 a cubic face-centered CFC type of crystalline spinel (Andrews KW , Dyson DJ 1967)
292 and that confirmed the XRD results.

293 *Fig. 7 SEM (a) TEM (b) Diffraction pattern (c) of nanoparticles CoBi_2O_4 .*

294 The elementary study of the CoBi_2O_4 nanoparticles was carried out by Energy
295 Dispersive X-ray spectrometer (EDX). The peaks for Co, Bi and O elements were
296 clearly observed in the EDX image, as shown in figure 8 (a). The atomic percentage of
297 the elements in the sample are given in the inset Table of the EDX data. The atomic
298 percentages of Co, Bi and O were estimated to be 14.02%, 26.25% and 59.73%,
299 respectively. The quantification of Co, Bi and O confirmed that the atomic ratio of
300 Co:Bi:O was 1.00:1.87:4.26, which agrees with the theoretical stoichiometric
301 composition of CoBi_2O_4 .

302 X-ray fluorescence measurements (XRF) spectra figure 8 (b) showed that Co
303 and Bi were the most abundant elements. Regarding silver (Ag), it was used in the
304 XRF analysis method. The inset Table of the XRF results shows that the weight
305 percentage of CoO and Bi₂O₃ was estimated to be (14.109%) for CoO and (85.89%)
306 Bi₂O₃. The molar mass was then calculated for CoO and Bi₂O₃ and found to be 74.93
307 and 467.96 g/mol, respectively. This confirmed that the atomic ratio of Co:Bi:O was
308 1.00:1.95:3.93, which agrees with the theoretical stoichiometric composition of
309 CoBi₂O₄ and also in line with the EDX analysis.

310 *Fig. 8 Energy dispersive X-ray (a) X-ray fluorescence (b) diffractogram of*
311 *nanoparticles CoBi₂O₄.*

312 The elemental mappings in figure 9 were located in the same EDX region. The
313 colored map of the SEM image (where Co, Bi and O are given in colors like Green,
314 Red and Blue, respectively) revealed that Co, Bi, and O elements coexisted and were
315 uniformly distributed.

316 *Fig. 9 EDX elemental mapping images of CoBi₂O₄ a) All elements b) Cobalt c)*
317 *Bismuth d) Oxygen.*

318 Optical properties of CoBi₂O₄ nanostructure were measured using the UV–Vis
319 diffuse reflectance spectrum. As shown in figure 10, the bandgap was estimated as
320 2.5 eV which is lower than that of TiO₂ and ZnO (3.2 eV) (Serpone 2006; Miki-yoshida
321 2016). This indicates that CBO has an excellent absorption level in the wavelength
322 range from 300 to 800 nm that contains both UV and visible light, which appears more
323 efficient than ZnO and TiO₂, leading to an increase in the formation of electron-hole
324 pairs on the photocatalyst's surface in visible light irradiation.

325 *Fig. 10 UV–Vis optical absorption edges.*

326 3.2 Artificial neural network modeling of the elimination of Cefixime

327 For the modeling, irradiation time, pH, initial CFX concentration and CBO catalyst
328 dose were selected as the input variables and the related degradation rate of CFX was
329 the output variable. To feed the structure of the ANN, a total of 40 experimental sets
330 were used. The data sets have been divided into 70% training, 15% validation and
331 15% test, as shown in Table 2.

332 *Table 2 Data sets of experimental results and ANN's predicted results.*

333 The essential part of the neural network architecture is the choice of the number
334 of hidden neurons. The model's best performance comes when the mean square error
335 (MSE) determined using equation (2), is the smallest.

336 *Fig. 11 Impact of the number of hidden neurons on the MSE of the neural network.*

337 Figure 11 shows that the Levenberg-Marquardt with a training function 'trainlim'
338 and 13 hidden-layer neurons produced the highest correlation coefficient $R^2 = 0.996$
339 and the smallest MSE value 1.81×10^{-4} . The relation of experimental data to ANN
340 model predictions can be derived from the contrast between the experimental data and
341 the predictions of the ANN model (Fig.12). The training data were given as the model's
342 input values, and the simulation output was compared with the relevant experimental
343 data. The adaptation of the model results to experimental data for the training data set
344 was very successful. The main part of model validation is the testing of network
345 performance for the testing data set access, the correlation coefficient was likewise
346 very high in this case $R_{\text{test}}^2 = 0.977$.

347 *Fig. 12 The relation of experimental data to the ANN model's predictions for each*
348 *type of data.*

349 3.2.1 Effect of pH

350 The pharmaceuticals polluted water is discharged in the environment at variable
351 pH values; consequently, it is necessary to investigate the role of pH on the
352 photocatalytic degradation. For this purpose, photodegradation experiments have
353 been carried out in 100 ml of 10 mg/L CFX solution at a fixed CBO amount of 0.1 g
354 and 360 min irradiation. Three different initial pH was selected and kept constant by
355 adding HCl or NaOH. The degradation rate of CFX increased with the increase of the
356 pH value of the solution from 4 to 6 and then decreased from 6 to 8, as observed in
357 figure 13 (a). Based on these results, it can be deduced that the photodegradation of
358 CFX was optimal at pH = 6. It is difficult to grasp pH impact on the performance of the
359 photocatalytic degradation process because of its multiple roles, such as the neutral
360 electrical charge of the CFX molecules, as well as the protonation and the
361 electropositive surface of CBO. This may also be related to the reaction between
362 organic compounds and dissolved oxygen (Abbasi and Hasanpour 2017). The
363 improvement of the photocatalytic activity of the catalyst at pH = 6 can probably be
364 related to the charge accumulation on the external surface (Bai et al. 2017). So, the

365 pH change may therefore affect the dispersion of the catalyst in the suspension.
366 Moreover, figure 13 (b) shows that the values predicted by the ANN model were well
367 in line with the experimental data.

368 3.2.2 Effect of the catalyst dose

369 The effect of CBO catalyst dose on the photodegradation activity of CFX was
370 examined. A set experiment was conducted by using a catalyst dose ranging from 0.05
371 to 0.15 g in 100 mL of solution for 15 mg/L of CFX at pH = 6 and 360 min irradiation.
372 Figure 13 (c) illustrates the effect of the catalyst dose on the CFX photodegradation
373 removal, showing that the degradation of CFX increased from 66% to 72% for an
374 increase of the catalyst dose from 0.05 to 0.08 g because of the limited active sites
375 available on the CBO catalyst surface. However, the degradation efficiency of CFX
376 decreased beyond this amount of catalyst, namely from 0.08 to 0.15 g. This may be
377 attributed to the fact that the accumulation of free catalysts leads to an increase in the
378 opacity of the solution and a decrease in light penetration. This is due to a scattering
379 effect for an expansion of the dose of catalyst (Zhou et al. 2018). Therefore, the optimal
380 dosage of the catalyst for CFX photodegradation was selected to be 0.08 g. Based on
381 the obtained results shown in figure 13 (d), the results predicted by the ANN and the
382 experimental values were well agreed.

383 3.2.3 Effect of the initial CFX concentration

384 For the purpose, the photodegradation studies were performed by varying initial
385 concentrations of CFX from 5 to 15 mg/L in 100 ml of the solution with 0.1 g of the CBO
386 catalyst at pH 6 after 360 min of irradiation time under visible light. Figure 13 (e) shows
387 that by raising the CFX concentration, the degradation yield decreased from 82 to 55%.
388 This behavior can be related to the diminishing number of available sites on the catalyst
389 CBO surface. Therefore, a high number of CFX molecules would have an inhibitory
390 effect on the photodegradation efficiency due to the lack of any direct contact between
391 the CBO catalyst surface and CFX. Besides, many photons could be absorbed by the
392 CFX molecules and hence did not reach the catalyst surface. The comparison between
393 ANN predicted values and the experimental data shown in figure 13 (f) revealed a good
394 agreement between them.

395 *Fig. 13 (a) effect pH (c) effect of catalyst dose (e) effect of initial CFX concentration*
396 *(b,d,f) Comparison of the experimental results with the predicted ANN values for*
397 *various operating parameters.*

398 3.2.4 The relative significance

399 An evaluation process based on the network weight matrix and the Garson's
400 equation (Garson 1991) was applied to calculate the relative significance of the input
401 variables on the network's output. The relative significance of input variables
402 influencing the CFX photodegradation values has been calculated by equation 6
403 (Ibrahim 2013).

$$RI_X = \sum_{x=1}^n \frac{|w_{xy}w_{yz}|}{\sum_{y=1}^m |w_{xy}w_{yz}|} \quad (6)$$

404 where RI_X is the relative significance, n and m are respectively the input numbers and
405 hidden neurons. w_{xy} are the connection weights, $\sum_{y=1}^m |w_{xy}w_{yz}|$ is the sum of the
406 product of the final weights of the connections from input neurons to hidden neurons
407 along with the links from hidden neurons to output neurons (Ibrahim 2013).

408 *Table 3 ANN model's weight and bias matrix.*

409 The ANN model's weight matrix is given in Table 3, while the relative significance of
410 the input variables derived from equation (4) is displayed in figure 14. As can be seen,
411 the initial CFX concentration showed the most significant impact on the performance
412 of CFX photodegradation (28%) compared with the other operating factors, namely
413 CBO dosage (27%), irradiation time (24%) and pH (21%).

414 *Fig. 14 The relative significance of the inputs on CFX degradation.*

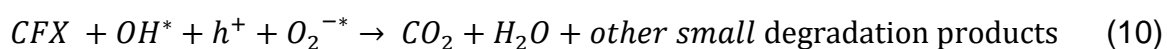
415 3.3 Effect of scavenging agents and the photocatalytic mechanism

416 Generally, the photodegradation of organic compounds by a catalyst semi-
417 conductor can be described by different reaction pathways regulated by different active
418 species such as OH^\bullet hydroxyl radical, superoxide O_2^\bullet , and photogenerated electrons
419 and holes e^-/h^+ pairs which called reactive oxidant species (ROS) (Zuo et al. 2017).
420 To investigate the dominant ROS on the photodegradation of Cefixime over the CBO
421 catalyst and for an understanding of the photocatalytic mechanism, several active
422 species trapping tests were run in the presence of different concentrations of some

423 scavengers. Each of the scavenging species was chosen for a specific type of
 424 photocatalytic radicals. p-Benzoquinone BQ was used as superoxide O_2^{\bullet} radical
 425 quencher (a scavenger for superoxide anion radical) (Nithya and Ayyappan 2020),
 426 Potassium dichromate $K_2Cr_2O_7$ was used as a scavenger for electron (e^-) (Gupta et
 427 al. 2020), Disodium ethylenediaminetetraacetic acid (Na_2 -EDTA) was used as a
 428 scavenger for the hole (h^+) and as photoinduced h^+ acceptor (Tho et al. 2020) and
 429 isopropanol (IPA) alcohol was employed as an OH^{\bullet} scavenger (hydroxyl OH^{\bullet} radical
 430 quencher) (Ghattavi and Nezamzadeh-Ejhih 2020). The tests were performed with
 431 an initial Cefixime concentration of 5 mg/L, at pH 6, and using CBO with a solution ratio
 432 of 0.8 g/L. The impact of these scavenging agents (quenchers) on the
 433 photodegradation efficiency of CBO nanocomposite was shown in Fig 15.

434 *Fig. 15 Effect of different scavengers on photocatalytic degradation of CFX over CBO*
 435 *photocatalyst.*

436 The obtained results are summarized in the next order of the photodegradation
 437 efficiency in the presence of different scavengers: Sample without the scavengers
 438 (Free) (79 %) > $K_2Cr_2O_7$ (64%) > p-Benzoquinone (59%) > Na_2 -EDTA (40%) >
 439 Isopropanol (25%). As shown, the most decrease in the degradation efficiency was
 440 observed by Isopropanol which confirmed that the generated OH^{\bullet} has a dominant role
 441 in the degradation of CFX. OH^{\bullet} radicals are strong, active and unselected oxidizing
 442 species for organic substrates in terms of oxidative degradation (Kumar et al. 2020).
 443 Then it comes Na_2 -EDTA, this indicates that both OH^{\bullet} and h^+ are the major active
 444 species. However, in the presence of p-Benzoquinone, only a small effect has been
 445 observed on the CFX photodegradation. This indicates that O_2^{\bullet} was a minor active
 446 species. The effect of $K_2Cr_2O_7$ was so small that it neglected the electron e^- role in the
 447 CFX degradation. According to these results, the following pathways (Fig. 16 and
 448 equations 7,8,9 and 10) were suggested for the photodegradation of CFX onto CBO.



449 *Fig. 16 Proposed mechanism for CFX degradation in the presence of $CoBi_2O_4$*
 450 *nanoparticles.*

451 3.4 Comparison of Cefixime photodegradation by different processes

452 In order to enhance the photocatalytic performance of CFX by synthesized CBO
453 nanoparticles and also to eliminate the photolysis effect, a set of experiments have
454 been tested in the same condition as illustrated in fig.17. The experiment was
455 conducted in the presence of 0.1 g catalyst at pH 6, room temperature and an initial
456 CFX concentration of 10 mg/L. In the absence of the catalyst, a very small degradation
457 rate of CFX by photolysis can be observed, lower than 5%. On the other hand, in the
458 presence of the CBO photocatalyst, the degradation rate of CFX reached 60 % within
459 3 h. The hetero-systems can increase the rate of photo-activity by extending the
460 spectral photo response of wide band semiconductors toward the visible light region,
461 as already demonstrated in recent works (Belaissa et al. 2016; Boumaza et al. 2016;
462 Rekhila et al. 2017; Boutra et al. 2019). For that, the new hetero-system $\text{CoBi}_2\text{O}_4/\text{ZnO}$
463 has been tested. Different weight ratios of the two catalysts CBO and ZnO were tested
464 to examine the impact on the CFX photodegradation. As can be seen in fig.17, the high
465 photodegradation efficiency was noticed at ratio of 50%/50% weight percentage of the
466 hetero-system $\text{CoBi}_2\text{O}_4/\text{ZnO}$, leading to an 80% degradation efficiency within only 3 h.

467 *Fig. 17 Time-course of the CFX degradation by different processes.*

468 4. Conclusion

469 In summary, in the present work, CoBi_2O_4 nanoparticles were successfully
470 synthesized by the sol-gel method and then characterized by both spectroscopic and
471 morphological tools. The catalysts prepared were tested for CFX antibiotic
472 degradation. The photocatalytic degradation of CFX was modeled successfully using
473 an artificial neural network (ANN). A feed-forward neural network with backpropagation
474 method and a Levenberg-Marquardt method was used. The degradation of CFX in
475 different operating conditions was predicted with 13 hidden neurons. The results
476 showed that the CoBi_2O_4 nanoparticles led to an 86 % CFX photodegradation yield in
477 the following optimal condition, pH = 6, 5 mg/L CFX, 0.8 g/L catalyst dose and 360 min
478 of irradiation. It was shown that all the parameters of the study (irradiation time, pH,
479 initial concentration of CFX and catalyst dose) have a significant effect on the CFX
480 photodegradation.

481 However, the main effect was the CFX's initial concentration. Moreover, the effects
482 of some scavenging agents were studied and the results confirmed the dominant role

483 of hydroxyl radical OH• in the CFX degradation process. Finally, the new CoBi₂O₄/ZnO
484 hetero-system was discussed and demonstrated a rapid degradation efficiency of 80
485 % in just 3 hours. Owing to these promising preliminary results, it will be further
486 considered in future works.

487 **Acknowledgment**

488 The authors gratefully acknowledge the financial support from the Thematic
489 Research Agency for Science and Technology (ATRST) through the national research
490 program (PM, PRFU Project N°A16N01UN160420190002) and the Directorate-
491 General for Scientific Research and Technological Development (DGRSDT) of Algeria.

493 **Declaration**

494

495 **Ethics approval and consent to participate**

496 Not applicable

497

498 **Consent for publication**

499 Not applicable

500

501 **Competing interest**

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

503

504 **Authors contributions**

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

507 *Noureddine Nasrallah and Aymen Amin Assadi*: conceptualization, funding acquisition,
508 methodology, resources, project administration, supervision, writing-review and
509 editing.

510 *Phuong Nguyen-Tri*: writing-review and editing, methodology, conceptualization.

511 *Bouzid Guedioura*: formal analysis

512 *Abdeltif Amrane and Sonil Nanda*: investigation, visualization.

513

514 **Availability of data and materials:**

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

517

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718

Table 1 ANN model parameters.

Parameters	Value
Input Neurons	pH, time, dose CBO, concentration of CFX
Output Neurons	Degradation of CFX
Number of Hidden Layer	(2-20) selection based on minimum MSE
Training function	Levenberg-Marquardt
Number experiment points	40 points
Performance function	MSE
Data division	70%-15%-15%

Table 2 Data sets of experimental results and ANN's predicted results.

Run	Time (min)	pH	CFC (ppm)	photocatalyst (g/l)	photodegradation (%)	
					Actual	Predicted
1	30	6	10	1	0.1281	0.1303
2	360	6	15	1	0.5471	0.5501
3	120	6	10	1	0.4812	0.4831
4	30	6	15	0.75	0.1065	0.1087
5	240	6	10	1	0.6813	0.6816
6	240	6	12.5	1	0.5814	0.5742
7	360	6	10	1	0.7031	0.699
8	60	6	15	1.5	0.1238	0.1229
9	240	4	10	1	0.5378	0.5382
10	300	8	10	1	0.6216	0.6205
11	360	8	10	1	0.6445	0.6484
12	300	6	15	1.5	0.4857	0.4864
13	180	4	10	1	0.4538	0.454
14	300	6	15	0.75	0.5017	0.5027
15	60	4	10	1	0.1387	0.1403
16	120	6	15	1.5	0.2286	0.2286
17	360	4	10	1	0.5588	0.5753
18	120	6	15	0.5	0.3464	0.3529
19	360	6	15	1.5	0.5238	0.5521
20	60	6	12.5	1	0.2093	0.2002
21	180	6	15	0.5	0.3954	0.4005
22	120	6	15	1	0.3134	0.3162
23	120	6	15	0.75	0.3471	0.3442
24	360	6	15	0.5	0.4444	0.4585
25	300	6	15	0.5	0.45	0.4448
26	360	6	15	0.75	0.502	0.504
27	300	6	15	1	0.538	0.5336
28	60	8	10	1	0.1972	0.1965
29	60	6	15	1	0.183	0.1828
30	180	8	10	1	0.4954	0.4832
31	60	6	5	1	0.4468	0.4464
32	300	4	10	1	0.5588	0.5592
33	240	6	15	1	0.4928	0.503
34	30	6	5	1	0.1844	0.282
35	240	6	5	1	0.8227	0.8208
36	300	6	10	1	0.6969	0.7056
37	360	6	5	1	0.8227	0.824
38	180	6	10	1	0.6	0.6174
39	60	6	15	0.5	0.2647	0.2456
40	60	6	10	1	0.2469	0.2497

Table 3 ANN model's weight and bias matrix.

Neurons of hidden layer	Weights and biases between input and hidden layers					Weights and biases between hidden and output layers	
	Input variables					Output Degradation Rate %	Bias
	Radiation time	pH	Initial concentration of CFX	Catalyst dosage	Bias		
1	-0.209	-0.155	-2.371	-1.364	2.586	0.258	
2	-0.524	-1.142	-1.34	-1.544	2.318	-0.514	
3	-1.669	1.438	1.281	-1.376	1.922	0.081	
4	1.204	1.295	-1.615	0.709	-0.558	0.515	
5	-1.58	0.183	1.387	-1.792	1.284	0.217	
6	-1.005	-1.551	-1.256	1.273	0.359	0.117	
7	1.407	-1.721	-0.843	-0.515	-0.531	-0.157	-0.29
8	-0.0028	-1.191	-1.811	-0.459	-0.645	0.3	
9	-1.107	-1.116	-0.201	-1.503	-0.872	-0.277	
10	-0.5608	1.804	-0.763	1.813	-1.227	-0.721	
11	2.053	0.782	-0.303	-0.83	1.619	0.71	
12	1.637	-0.136	-1.36	-1.151	2.809	-0.614	
13	1.435	0.1417	-1.93	-1.541	2.271	0.231	

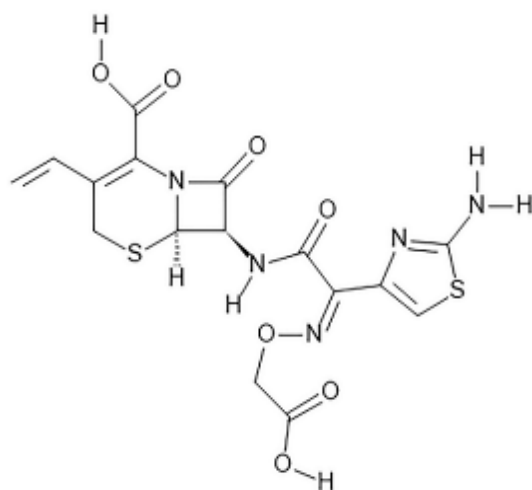


Fig. 1

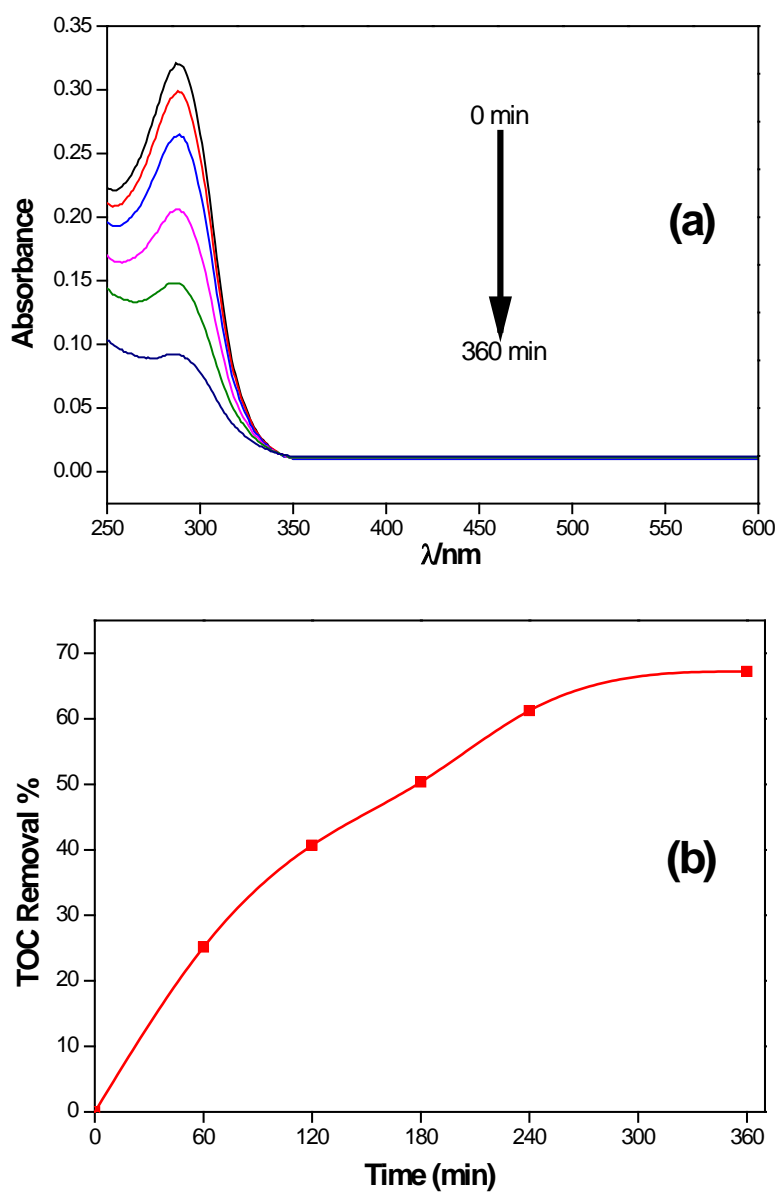


Fig. 2

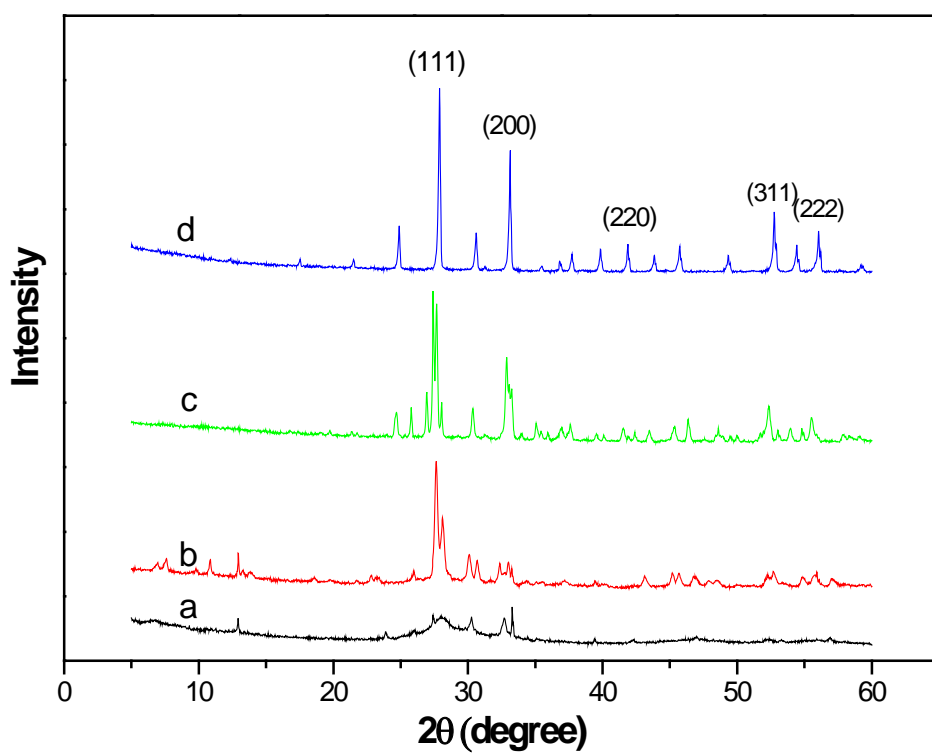


Fig. 3

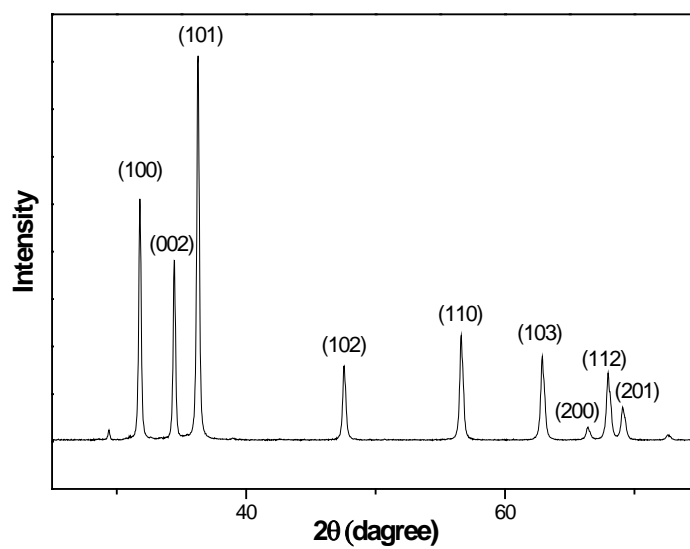


Fig. 4

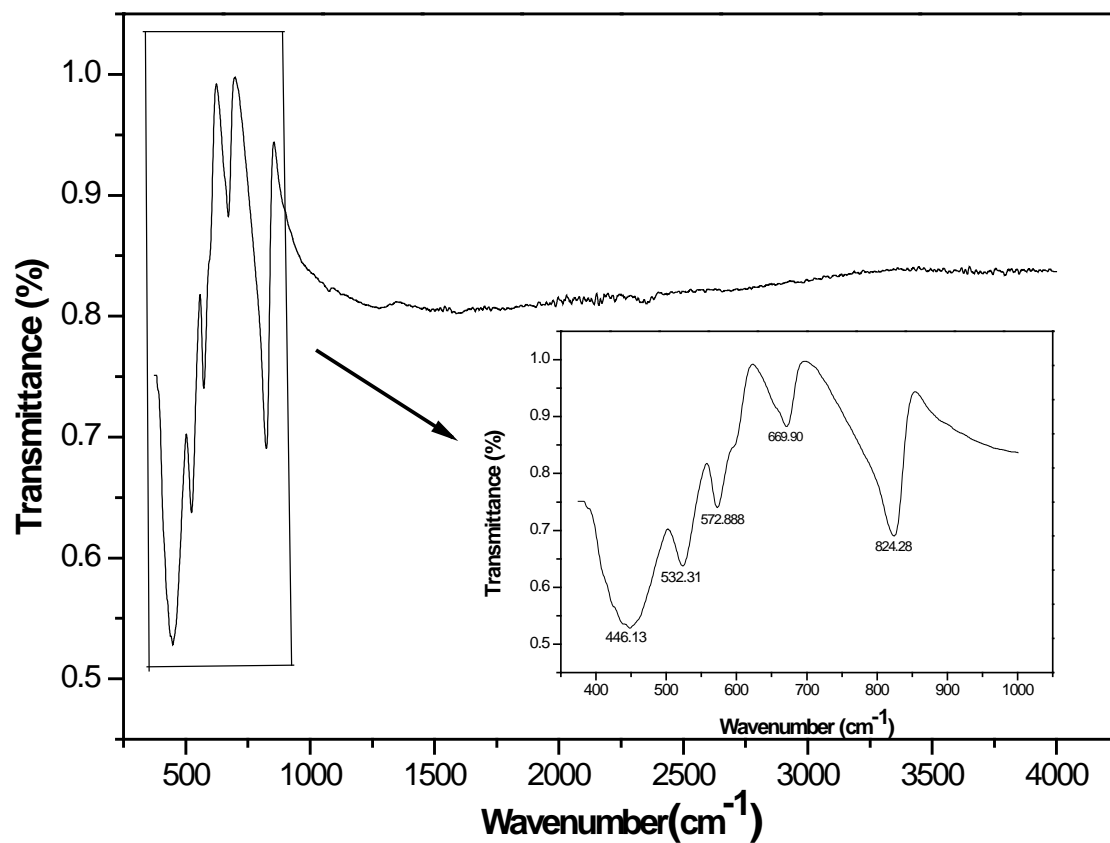


Fig. 5

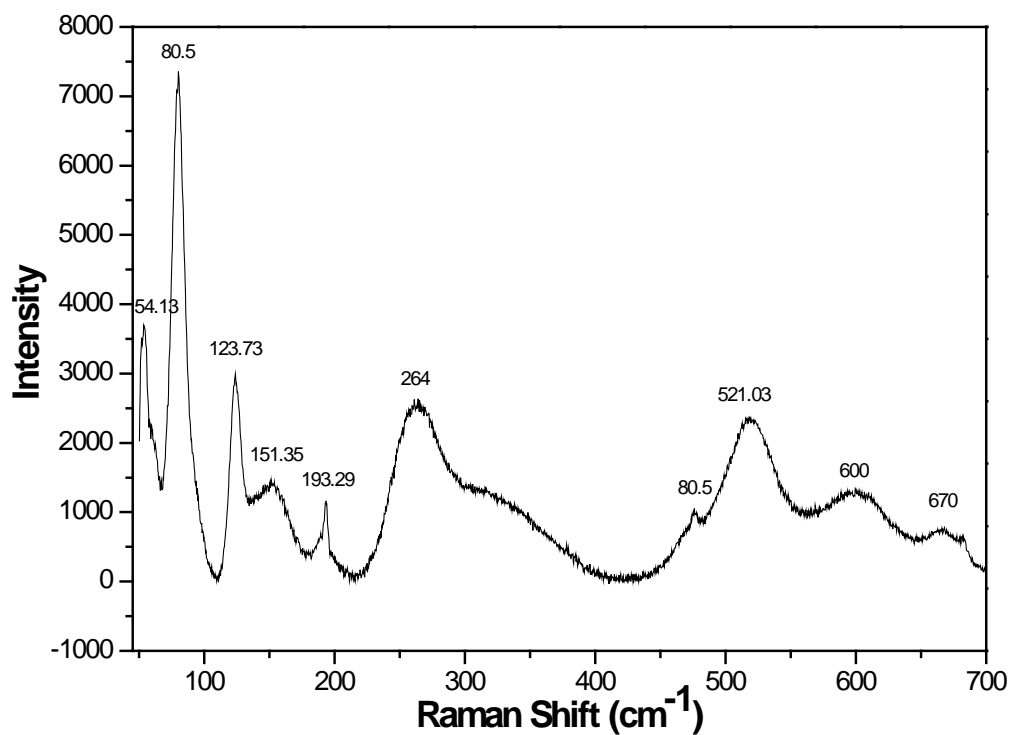


Fig. 6

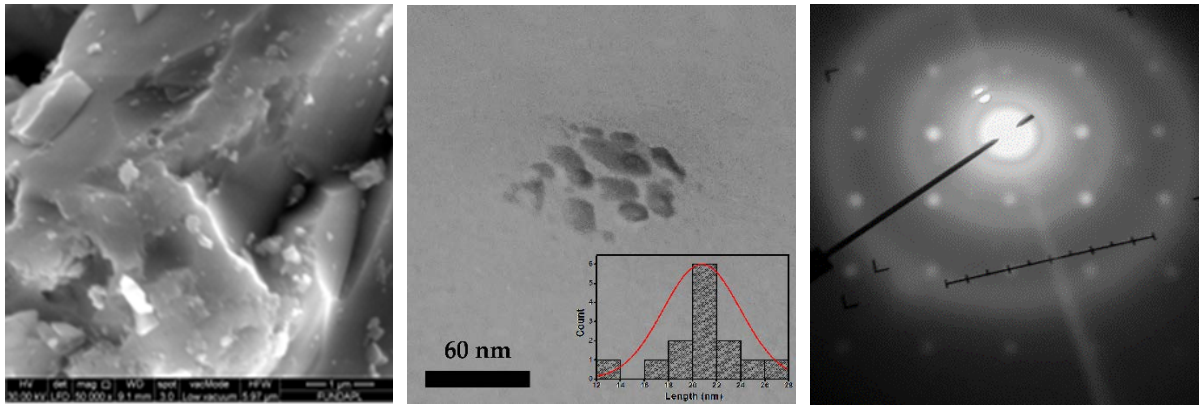
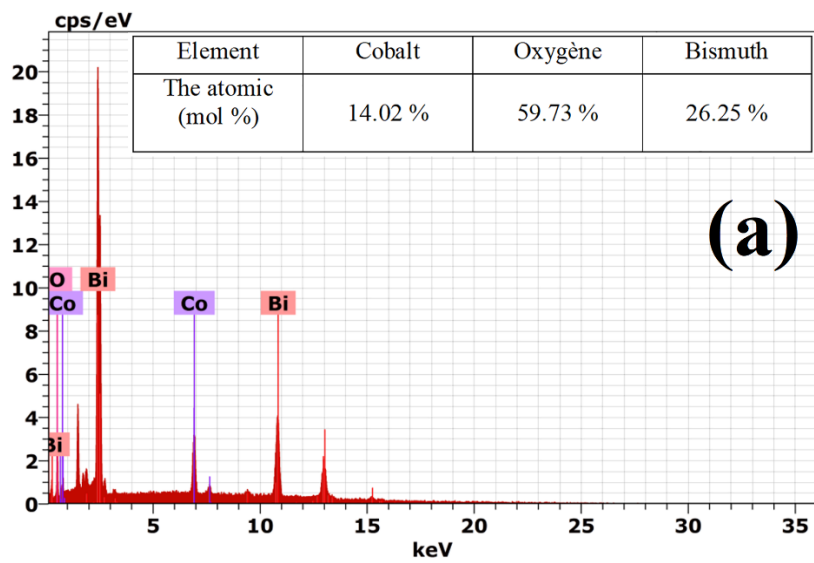
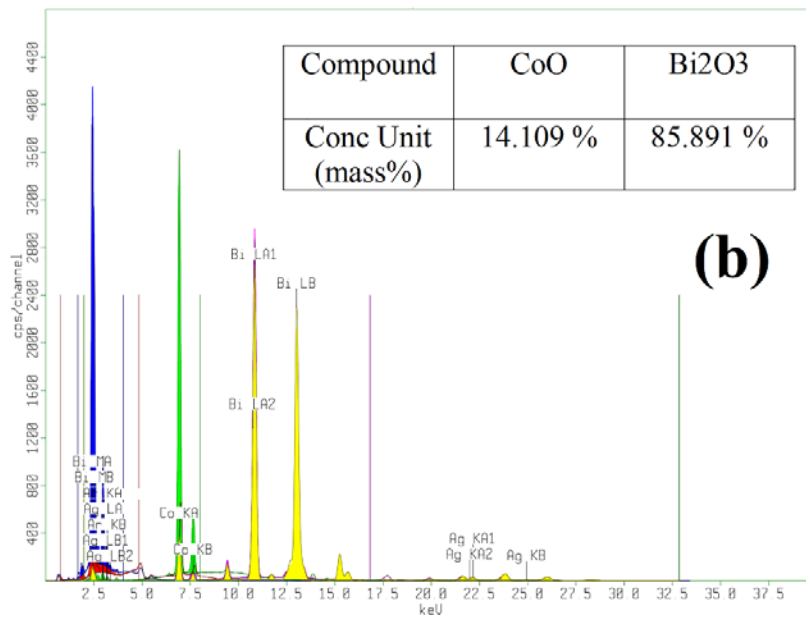


Fig. 7



(a)



(b)

Fig. 8

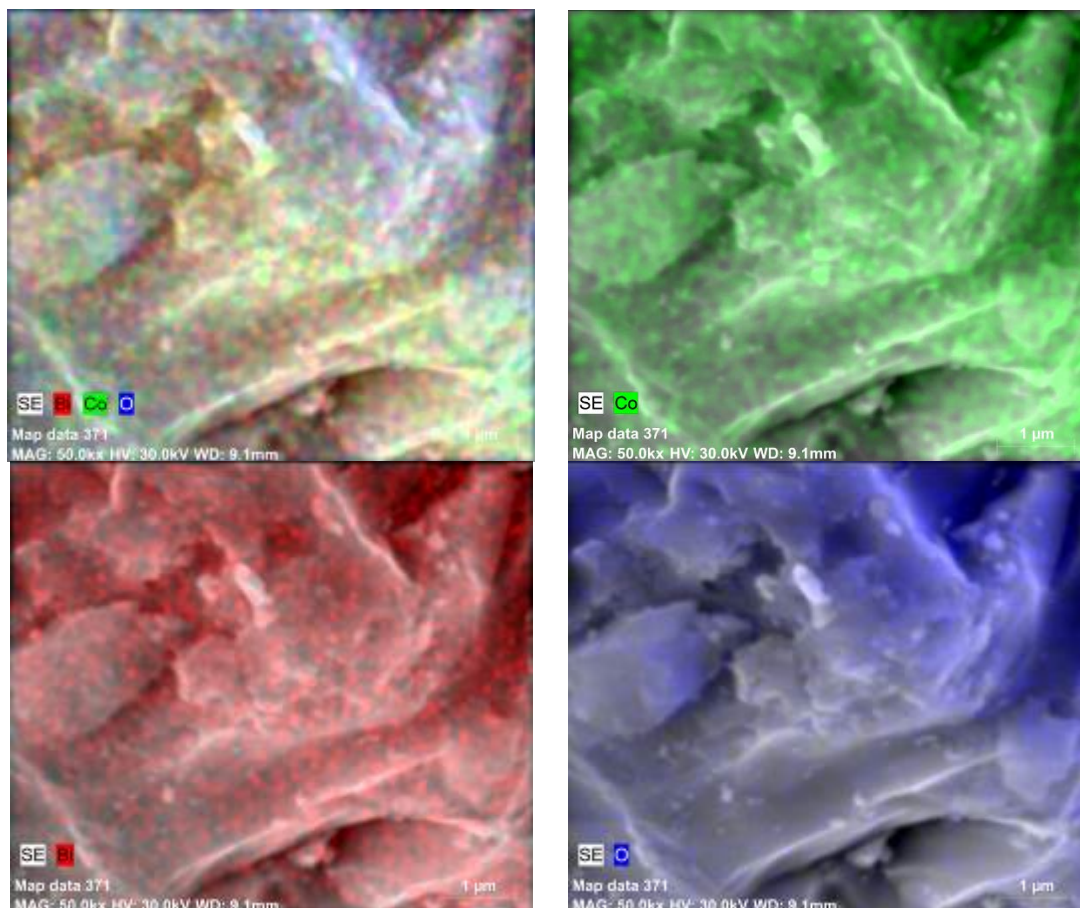


Fig. 9

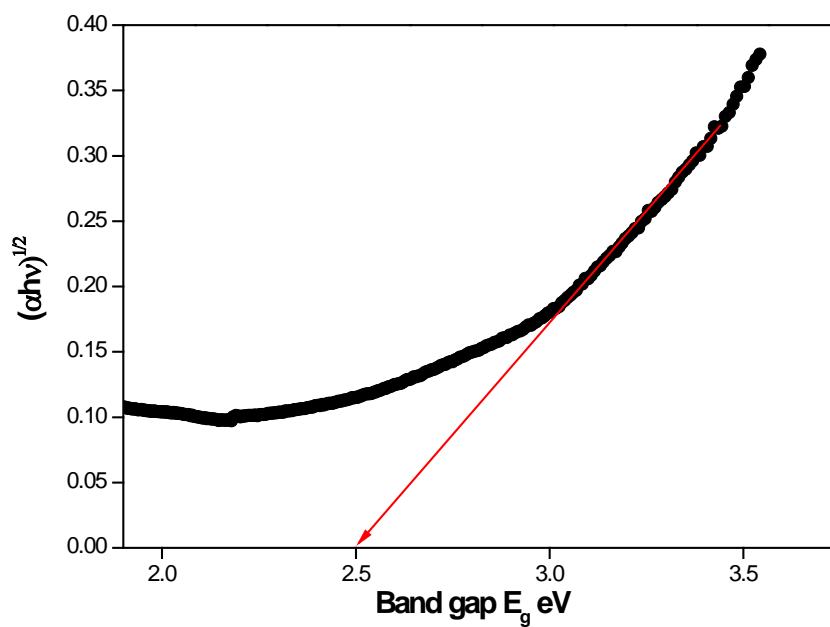


Fig. 10

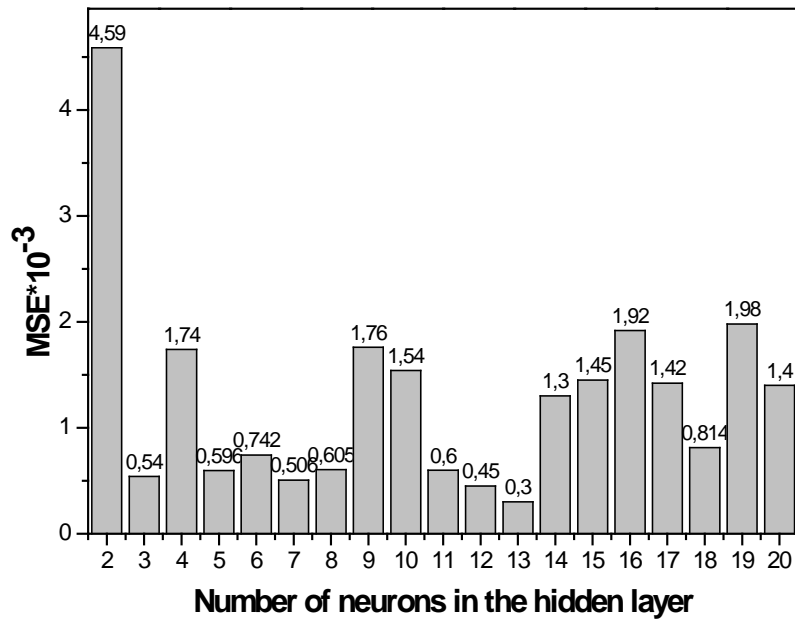


Fig. 11

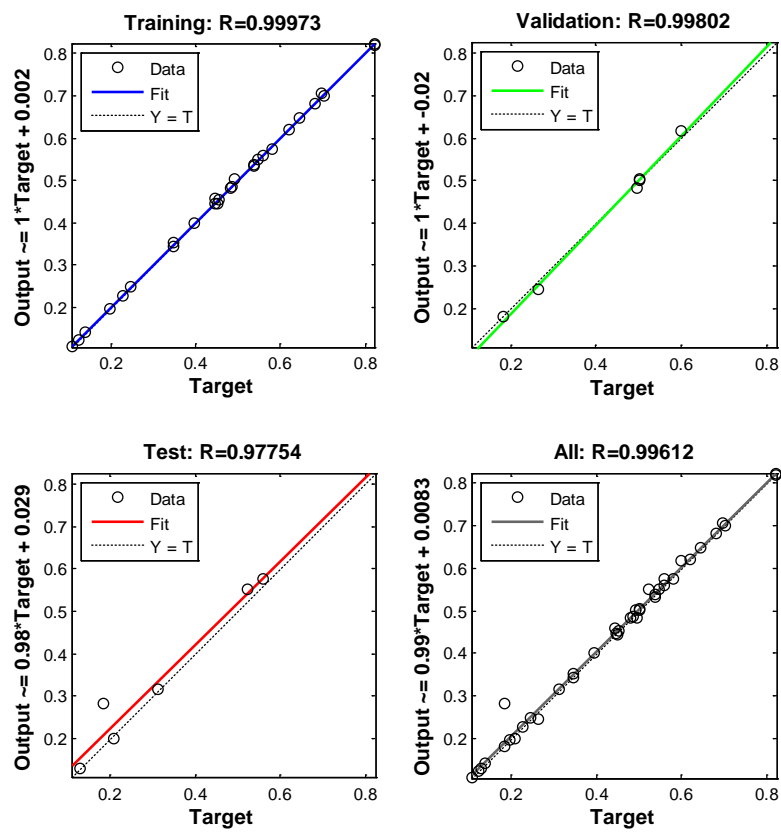


Fig. 12

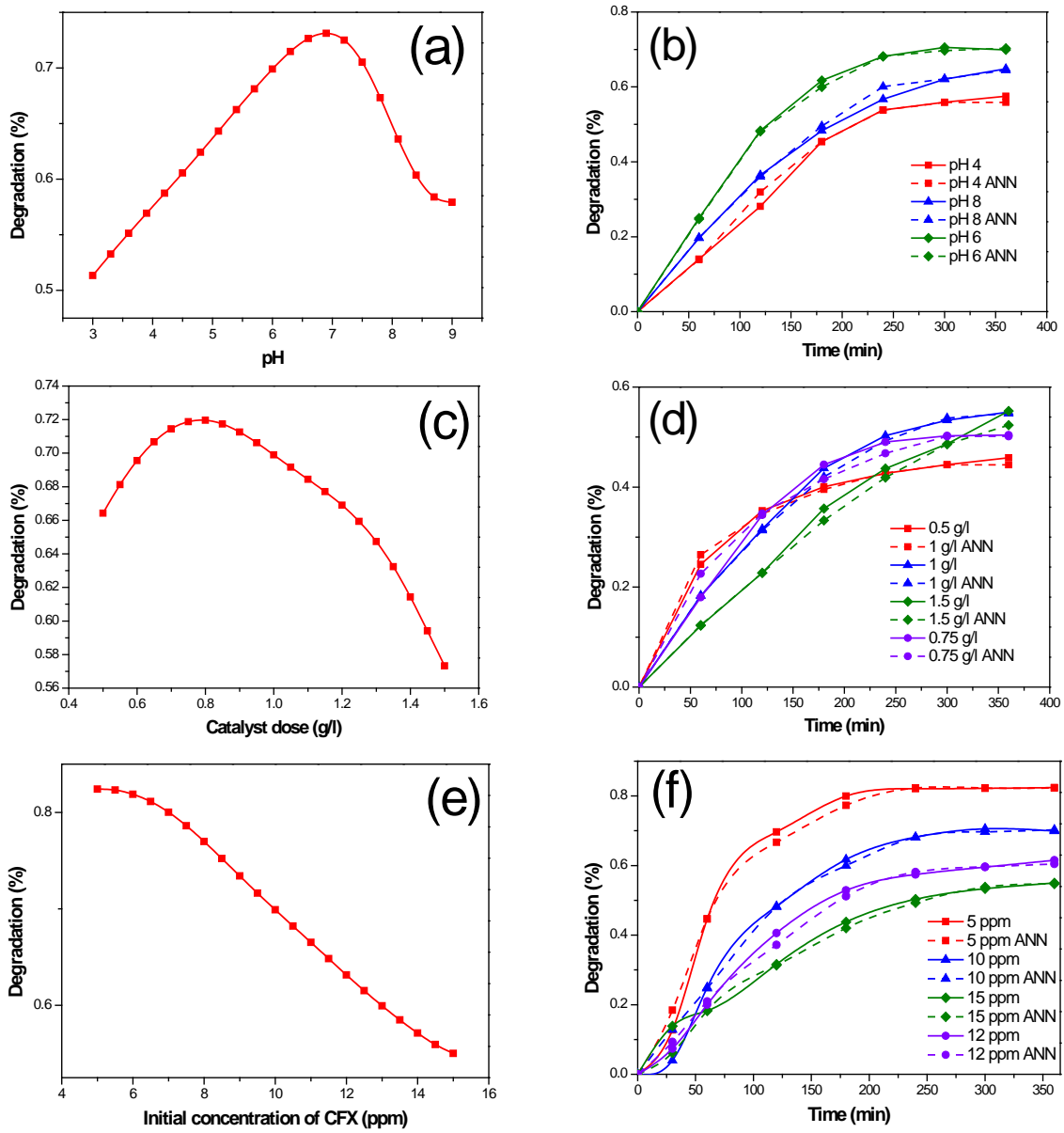


Fig. 13

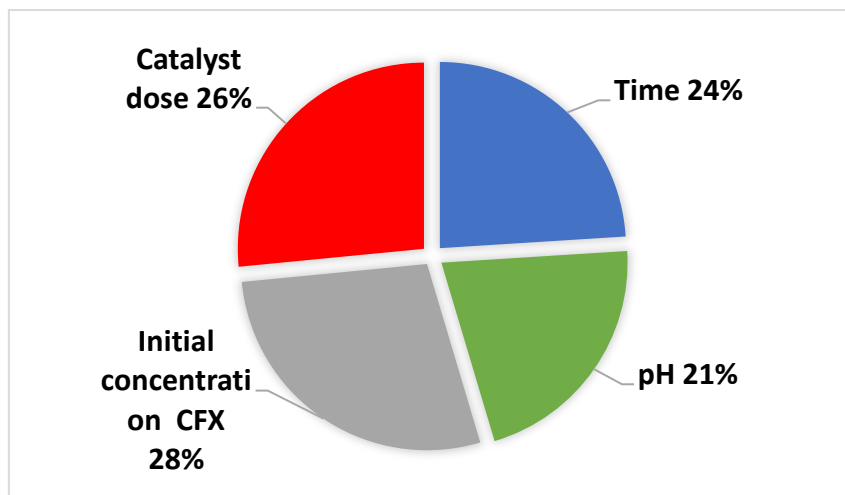


Fig. 14

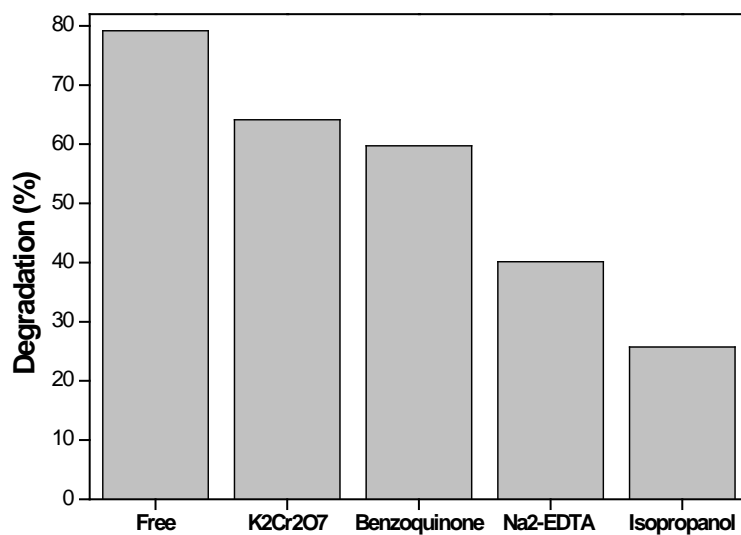


Fig. 15

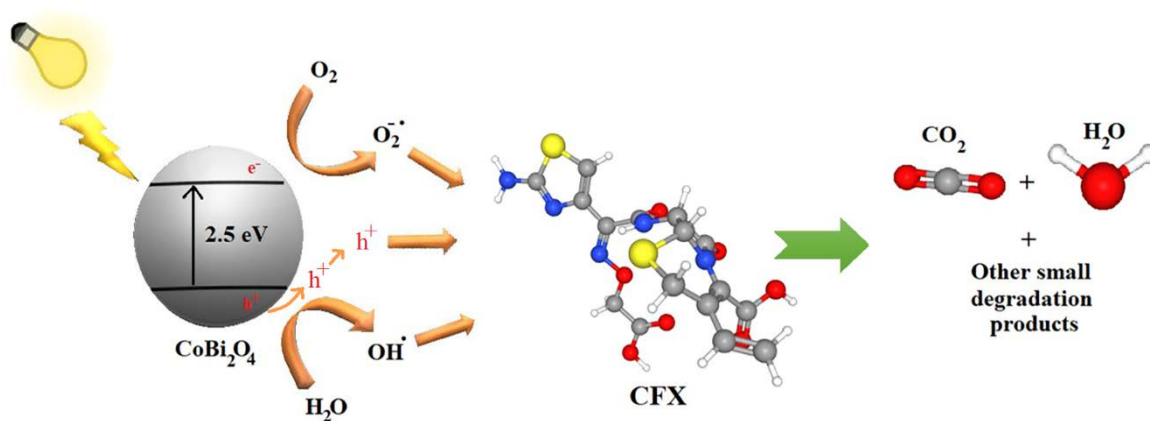


Fig. 16

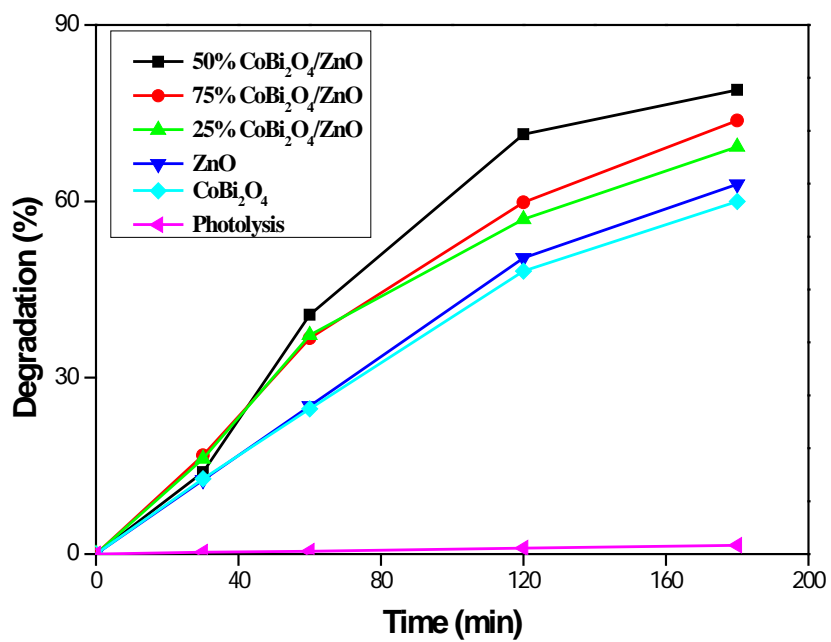


Fig. 17