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1 **Use of laterite as a sustainable catalyst for removal of**
2 **fluoroquinolone antibiotics from contaminated water**

3
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26 **Abstract**

27 Although there is a growing interest in Fenton oxidation processes based on natural catalysts,
28 the use of laterite soil to promote sequential adsorption/oxidation treatments of
29 fluoroquinolone antibiotics has been scarcely investigated. In this work, the ability of an
30 african laterite containing goethite and hematite to remove flumequine (FLU), used as a
31 representative compound of fluoroquinolone antibiotics, was evaluated under dark and UVA
32 irradiation. Batch experiments and liquid chromatography analyses showed that the presence
33 of laterite can enhance FLU removal from heavily contaminated water through both sorption
34 and oxidation reactions (up to 94% removal of 77 $\mu\text{mol L}^{-1}$ of FLU and 72% of
35 mineralization). The heterogeneous reaction rate is dominated by the rate of intrinsic surface
36 chemical reactions including sorption and oxidation of FLU, and light-induced reduction of
37 Fe^{III} sites to produce Fe^{II} . Based on the probe and scavenging experiments, $\bullet\text{OH}$ radicals were
38 mainly involved in the heterogeneous oxidation reaction. The photo-assisted Fenton process
39 showed a high efficiency of FLU removal even in the presence of a second fluoroquinolone
40 antibiotic, norfloxacin (NOR), which can be co-found with FLU in affected environments.
41 Determinations of kinetic rate constants and total organic carbon (TOC) for five sequential
42 adsorption/oxidation cycles showed that laterite exhibited no deactivation of surface sites and
43 an excellent catalytic stability. This cost-effective and environmentally friendly remediation
44 technology may appear as a promising way for the removal of fluoroquinolone antibiotics
45 from multi-contaminated waters.

46

47 **Keywords:** Laterite; fluoroquinolone antibiotics; sorption; oxidation; stability; UVA
48 irradiation.

49

50

51 **1. Introduction**

52 Fenton reaction based on generation of highly reactive oxygen species (ROS) has attracted
53 continuous attention during the past decades, and is considered as a powerful oxidative
54 method for the treatment of persistent organic pollutants (Anipsitakis and Dionysiou 2004;
55 Pignatello et al. 2006). In homogeneous Fenton process, dissolved iron and H₂O₂ are used to
56 produce ROS (Anipsitakis and Dionysiou 2004; Pignatello et al. 2006). In heterogeneous
57 system, iron oxy-hydroxides, iron bearing minerals and/or iron immobilized diverse supports
58 are generally used to promote the Fenton reaction (Lin and Gurol 1998; Kwan and Voelker
59 2003; Matta et al. 2007; Gonzalez-Olmos et al. 2009; Guo et al. 2010; Ghauch et al. 2011;
60 Gonzalez-Olmos et al. 2012; Wang et al. 2015; Lan et al. 2015). The latter process offers
61 many advantages over its homogeneous counterpart, such as no sludge formation, operation at
62 near neutral pH, easy separation/recovery of catalyst, etc. (Martínez et al. 2007 ; Gonzalez-
63 Olmos et al. 2009; Guo et al. 2010; Herney-Ramirez et al. 2010 ; Gonzalez-Olmos et al. 2012;
64 Minella et al. 2014). Because the decomposition rate of organic contaminants in
65 heterogeneous system is slower than in classic homogeneous Fenton reaction, different ways
66 have been developed to enhance the oxidation efficiency while keeping the benefits of
67 heterogeneous system. Among these processes, the photo-assisted Fenton reaction using light
68 energy can accelerate the reaction rate by decomposing H₂O₂ into most powerful oxidizing
69 species, and by reducing Fe^{III} to Fe^{II} and/or converting Fe^{III} back to Fe^{II} after the reaction
70 (Martínez et al. 2007 ; Herney-Ramirez et al. 2010 ; Gonzalez-Olmos et al. 2012; Minella et
71 al. 2014).

72 Different synthetic materials have been used as a catalyst in heterogeneous Fenton processes,
73 e.g. iron oxides (Matta et al. 2007; Minella et al. 2014; Wang et al. 2015), zeolite (Gonzalez-
74 Olmos et al. 2009; 2012), clay (Bohu et al. 2008; Herney-Ramirez et al. 2010), and modified
75 iron-carbon (Lan et al. 2015). However, the use of these materials for high-scale applications

76 in water and wastewater treatment may be limited due to their low effectiveness and/or high
77 costs (Garrido-Ramirez et al. 2010; Litter et al. 2017). Indeed, the high cost of supported or
78 composite catalysts leads the researchers to propose a cheaper alternative, particularly in the
79 developing countries.

80 Laterite soil is abundant in some parts of the earth including Africa. Although some studies
81 were dedicated to the use of laterite in Fenton reactions (Karale et al. 2013; Khataee et al.
82 2015), much remains to be learned on the sorption/oxidation activity of this mineral surface
83 and its catalytic stability. In addition, the binding and transformation mechanisms of organic
84 compounds interacted with laterite surfaces remain unclear.

85 This work aims to develop an effective heterogeneous Fenton process based on the use of a
86 natural catalyst and light source in order to effectively remove emerging contaminants from
87 contaminated water. FLU, an antimicrobial agent belonging to the second generation of
88 synthetic quinolones and frequently used in veterinary medicine (Gothwal and Shashidhar
89 2015), is selected here as a model of emerging pharmaceutical compounds. Due to its
90 continuous release into the environment and its persistence, 2.5-50 ng L⁻¹ (Pozo et al. 2006;
91 Tamtam et al. 2008) and 6.9 µg kg⁻¹ (Tamtam et al. 2011) of FLU residues have been
92 detected in aquatic environments and in the soil, respectively. To the best of our knowledge,
93 the removal of fluoroquinolone antibiotics using laterite soil as sorbent/catalyst was rarely
94 investigated. Here, the FLU removal was investigated at two pH values (pH 3 as an acidic pH
95 to ensure a high solubility of iron and pH 6.5, closer to near-neutral conditions of real
96 effluents) and with and without UVA irradiation. The influence of laterite loading and initial
97 concentrations of FLU and oxidant (H₂O₂) on the removal efficiency rate was also
98 investigated.

99 Higher concentrations of FLU than those encountered in real contaminated effluents were
100 used in order to test the removal capacity of laterite in heavily loaded contaminated waters,

101 *e.g.* multi-components contaminated water. Effect of co-occurring antibiotic on the FLU
102 degradation was also evaluated using norfloxacin (NOR), a fluoroquinolone antibiotic, which
103 can be co-found with FLU in affected environments (Tamtam et al. 2008). The Langmuir and
104 Langmuir–Hinshelwood models were used to describe the surface interactions with FLU in
105 the absence and the presence of oxidant (H₂O₂), respectively. Moreover, possible deactivation
106 of surface sites as well as the catalytic stability of laterite were assessed by conducting
107 sequential oxidation cycles, TOC measurements and solid characterization.

108

109 **2. Experimental**

110 **2.1. Materials**

111 Flumequine (99% purity), norfloxacin (99% purity), hydrogen peroxide (35% w/w), 1,10-
112 phenanthroline (>99% purity), sodium acetate (>99% purity), ferrous ammonium sulfate
113 hexahydrate ((NH₄)₂Fe(SO₄)₂·6H₂O), 2-propanol (C₃H₈O), and chloroform (CHCl₃) were
114 provided from Sigma–Aldrich. Solutions were prepared with high-purity water obtained from
115 a Millipore Milli-Q system.

116

117 **2.2. Laterite soil characterization**

118 Laterite soil was collected from Sinématialy town (9°34'60" N and 5°22'60" W) in the north
119 of Ivory Coast. The sample was grinded and passed through 250 μm sieve. The obtained
120 fraction was washed several times with pure water, and then dried at 50 °C.

121 In order to determine the crystal structure of natural mineral, sample of laterite (≤ 250 μm)
122 was analyzed by X-ray powder diffraction (XRD). The XRD data were collected with a D8
123 Bruker diffractometer, equipped with a monochromator and a position-sensitive detector. The
124 XRD peaks (Fig. S1) were attributed to quartz, goethite, hematite, kaolinite and gibbsite.
125 However, the most abundant phases in our sample are quartz, goethite and hematite, which is
126 in agreement with a previous work (Coulibaly et al. 2016). Consistently, the TEM-EDX

127 indicated a composition of Fe, Al and O (i.e. under oxide forms), together with two major
128 elements Ca and Mg (Fig. S1). More details are given in the supporting information. To
129 determine the metal contents in laterite, elements were analyzed using an inductively coupled
130 plasma atomic emission spectrometer (ICP-AES, Jobin-Yvon JY 70 Type HORIBA) after
131 acid digestion of the sample (Table S1). Potentiometric titrations of the laterite were
132 conducted in thermostated double walled pyrex cell at 293 K in 0.001, 0.01 and 0.1 M NaCl
133 solutions. The pH value of the suspensions was adjusted and kept constant with titrant
134 solutions (HCl or NaOH) at pH 3 or 6.5. The B.E.T. specific surface area and the Point Zero
135 Charge (PZC) of laterite soil were $23 \pm 1 \text{ m}^2 \text{ g}^{-1}$ and 6.5 ± 0.3 , respectively.

136

137 **2.3. Photoreactor and photodegradation experiments**

138 All experiments were performed in a 500 mL capacity batch photoreactor (made of
139 borosilicate glass) at room temperature ($20 \pm 2 \text{ }^\circ\text{C}$). The reactor was designed in a column
140 shaped in 34 cm high and 3.8 cm diameter. This setup has an enclosed chamber comprising a
141 reactor; an UVA lamp 24 W (Philips PL-L) placed in the center of the glass cell emitting in a
142 wavelength region 320–400 nm with emission peak centered at $\lambda_{\text{max}} = 360 \text{ nm}$, yielding a
143 irradiation intensity of 16 mW cm^{-2} as detected with a UVA Radiometer (VLX- 3W equipped
144 with a sensor CX 365, ALYS Technologies, Switzerland). The solution with catalyst was
145 continuously stirred with a magnetic bar at 180 rpm. The pH of the sample solution was
146 measured by means of VWR instruments 6000 pH-meter. Monitoring of suspension
147 temperature indicated no significant fluctuation ($20 \pm 2 \text{ }^\circ\text{C}$) along the experiment. The UV-
148 visible spectrum of FLU is shown in Figure S2.

149 Two different experiments were conducted at room temperature. In a first experiment, the
150 suspension of FLU and laterite was stirred in the dark for 4 h to reach the adsorption
151 equilibrium without UVA irradiation and oxidant (H_2O_2). In the second test, FLU, oxidant,
152 and laterite were mixed simultaneously under UVA irradiation. In both experiments, 500 mL

153 of a FLU solution of known concentration were prepared and the appropriate amount of
154 catalyst was added. In order to keep it constant, the pH of the solution was adjusted by HCl
155 and NaOH (0.1 M). Then, the required volume of H₂O₂ (35% w/w) was added to the solution.
156 At time intervals, 5 mL of the solution were collected and analyzed.
157 Aqueous organic compound concentrations were determined using a high performance liquid
158 chromatography (Waters 600 Controller) equipped with a reversed-phase C18 column (250
159 mm×4.6 mm i.d., 5 μm) and UV detector (Waters 2489). The detector was set to 246 nm for
160 FLU and 277 nm for NOR. The mobile phase was mixture of acetonitrile/water (20/80 v/v)
161 containing 0.1% formic acid. The flow rate was set at 1 mL min⁻¹ in isocratic mode. Total
162 Organic Carbon (TOC) was determined using a TOC-meter (Shimadzu TOC-VCSH) using 10
163 mL of solution. Total dissolved iron concentrations were measured by the 1,10-
164 phenanthroline method at 510 nm (Tamura et al. 1974). All these experiments were repeated 2
165 times and showed a good reproducibility with a standard deviation of 3%.

166 **3. Results and discussion**

167 **3.1. Preliminary characterization of removal capacity of the investigated laterite**

168 To characterize the sorption capacity of laterite, adsorption isotherms were determined at two
169 pH values (3 and 6.5) (Fig.1). Preliminary kinetic batch experiments conducted over 24 h
170 showed that equilibrium was achieved within 4 h of reaction time. The experimental isotherm
171 data were best fitted to the equation of Langmuir through linear regression ($r^2 = 0.99$). The
172 linear form of the Langmuir equation is given by:

$$173 \frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e \quad (1)$$

174 where q_m ($\mu\text{mol m}^{-2}$) is Langmuir maximum sorbed amount and K_a ($\text{L } \mu\text{mol}^{-1}$) is the
175 Langmuir isotherm constant. The progressive saturation of the surface sites shows that the
176 adsorption followed the Langmuir assumption with a maximum adsorption capacity of 1.40

177 $\mu\text{mol m}^{-2}$ at pH 3 and $1.19 \mu\text{mol m}^{-2}$ at pH 6.5. As typically encountered for anionic ligands,
178 FLU adsorption was greatest under acidic to circumneutral pH, and lowest under alkaline
179 conditions (See Fig. S3 for distribution of FLU species at various pH values). The K_a values
180 estimated from Langmuir model are $1.95 \text{ L } \mu\text{mol}^{-1}$ at pH 3 and $0.37 \text{ L } \mu\text{mol}^{-1}$ at pH 6.5.
181 The removal of FLU was then evaluated under different oxidation systems in presence and in
182 absence of laterite (Fig. 2). The heterogeneous process (*i.e.* UVA/H₂O₂/Laterite) showed the
183 best removal performance at both pH values, 77% and 62% of removal at pH 3 and 6.5,
184 respectively. In both experiments, the direct photolysis is less than 12%. To account for the
185 sorption on laterite, desorption tests (adding NaOH to have pH 11) were performed and total
186 amounts of FLU in aqueous phase were plotted against time (Fig. 2). The amounts of
187 degraded FLU lied at 56% at pH 3, and 43% at pH 6.5 and after 420 min of reaction time. It is
188 worth noting that pre-equilibration of FLU with laterite suspension for 4 h in the dark before
189 irradiation did not significantly change the kinetics behavior (Fig.S4). TOC measurements
190 over 540 min confirmed the oxidative degradation in UVA/H₂O₂/Laterite system, whereas
191 45% and 33% of mineralization was achieved at pH 3 and 6.5, respectively. As explained
192 below, optimization of experimental parameters improved the FLU degradation up to 94%,
193 and mineralization up to 72%.

194

195 The higher degradation performance at pH 3 may result from (i) changes in surface
196 interactions between FLU and laterite as more adsorption was observed at pH 3, (ii) high
197 formation rate of radical species at acidic pH (Buxton et al. 1988) and/or (iii) possible
198 leaching of Fe from laterite surfaces contributing to a homogeneous Fenton reaction. The
199 latter was excluded since the amount of iron leaching was found very low ($< 6 \mu\text{g.L}^{-1}$) even if
200 it is relatively higher at acidic pH than at pH 6.5 (Fig. S5). The possible release of trace

201 elements such as Cr, Cu, Co, Ni and Zn was also checked by ICP/AES, which indicated that
202 these elements were under quantification limits under our experimental conditions.

203 We note an increase of FLU degradation in UVA/H₂O₂/Laterite compared to UVA/H₂O₂
204 system. This improvement could be attributed to the higher generation of active species, e.g.
205 hydroxyl radicals and iron ferrous (Fe^{II}) (Martínez et al. 2007; Gonzalez-Olmos et al. 2012;
206 Minella et al. 2014). First, direct photolysis of H₂O₂ under UVA irradiation may generate
207 highly oxidizing species (*i.e.* •OH radicals). Moreover, the UVA irradiation may also enhance
208 the heterogeneous Fenton activity on the surface, by promoting the photo-assisted reduction
209 of Fe^{III} to Fe^{II}, which subsequently reacts with H₂O₂ generating •OH radicals. Therefore,
210 addition of H₂O₂ led to an acceleration of reaction rate, as compared to the UVA/Laterite
211 system, further confirming the synergetic effect of laterite and H₂O₂.

212

213

214 **3.3. Optimization of operating conditions**

215 The influences of H₂O₂ concentration, laterite dosage and initial concentration on the removal
216 of FLU were investigated at pH 3 and 6.5. The experiments, which were repeated 2 times,
217 showed a good reproducibility with a 5% of averaged standard deviation.

218 **3.3.1. Effect of H₂O₂ concentration**

219 Removal kinetics of FLU were determined at a wide range of H₂O₂ concentration (1 - 9 mmol
220 L⁻¹) and two pH values (3 and 6.5). The degradation of organic compounds by HO• is
221 typically described as a second-order reaction [1-6]:

$$222 \quad \frac{d[FLU]}{dt} = -k[FLU][HO\cdot] \quad (2)$$

223 where [HO•] is steady-state concentration of hydroxyl radical, [FLU] is concentration of FLU
224 in water, *k* is the second-order rate constant, and *t* is the reaction time. By assuming that HO•

225 instantaneous concentration is constant, the kinetics of degradation of FLU in water can be
226 described according to the pseudo-first-order equation as given below:

$$227 \quad [FLU]_t = [FLU]_0 \exp(-k_{app}t) \quad (3)$$

228 where k_{app} is the pseudo-first-order apparent rate constant (min^{-1}). k_{app} (min^{-1}) obtained by
229 linear regression of $\ln(C_t/C_0)$ versus time t , was plotted against H_2O_2 concentration. The k_{app}
230 constants were higher at pH 3 than pH 6.5. Since the degradation of FLU solution is directly
231 related to the concentration of hydrogen peroxide and formation of radicals, the removal
232 kinetic of FLU was enhanced when the H_2O_2 concentration increased from 1 to 4 mmol L^{-1} .
233 However, a decrease in k_{app} was observed at higher H_2O_2 concentrations (Fig. 3), thereby
234 suggesting scavenging effects of radicals by hydrogen peroxide ($k_{\text{H}_2\text{O}_2/\text{HO}^\cdot} = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$)
235 (Mechakra et al. 2016) and/or recombination of radicals (Buxton et al. 1988; Litter et al.
236 2017). At much higher H_2O_2 concentration, there is a competitive reaction between FLU and
237 H_2O_2 towards the reaction with ROS.

238 239 **3.3.2. Effect of laterite dosage**

240
241 The pseudo-first-order apparent rate constants (k_{app} (min^{-1})) were determined as previously
242 explained, and plotted against laterite loading (0.5 to 4 g L^{-1}) in Figure 4. As for previous
243 experiments, the observed pseudo-first order rate constant firstly increased with laterite
244 loading increasing and then reduced. This phenomenon can be explained by screening effects
245 occurring at high loading of solid in aqueous suspension, as previously reported for
246 heterogeneous photo-Fenton reactions (Bohu et al. 2008; Mechakra et al. 2016). In addition,
247 the generated radicals can be scavenged by metal oxide surfaces ($k_{\text{oxide}/\text{HO}^\cdot} = 8 \times 10^{11} (\text{g mL}^{-1})^{-1}$
248 s^{-1}) (Miller and Valentine 1999).

249 It is interesting to note that the optimal laterite loading of FLU removal is around 1 g L⁻¹
250 regardless of the tested pH ($k_{app} = 6.4 \times 10^{-3} \pm 0.0003 \text{ min}^{-1}$ and $4.6 \times 10^{-3} \pm 0.0003 \text{ min}^{-1}$ at pH
251 3 and pH 6.5, respectively).

252 253 **3.3.3. Effect of initial flumequine concentration**

254 The pseudo first-order rate constants (k_{app}) at various initial concentrations of FLU were
255 determined with the optimum conditions for laterite loading and oxidant concentration (Fig.
256 5). There is a decrease of k_{app} from $1.87 \times 10^{-2} \pm 0.0003$ to $6.2 \times 10^{-3} \pm 0.0003 \text{ min}^{-1}$ at pH 3 and
257 from $9.4 \times 10^{-3} \pm 0.0003$ to $4.1 \times 10^{-3} \pm 0.0003 \text{ min}^{-1}$ at pH 6.5 when FLU concentration
258 increased from 19 to 77 $\mu\text{mol L}^{-1}$. This expected phenomenon can be explained by the
259 competition of species (here FLU and H₂O₂) with each other for interactions with a fixed
260 number of active sites on solid surfaces. At higher FLU concentration, adsorption may occupy
261 a greater number of Fe^{III}-sites, which become unavailable to generate Fe^{II} upon irradiation
262 and/or interact with H₂O₂. This is consistent with previous works where photon absorption by
263 catalyst or photo-assisted reduction of surface sites to trigger the oxidation reaction is
264 considered as the rate-limiting step (Avetta et al. 2015). Furthermore, higher FLU
265 concentrations may lead to a decrease of photons entering into solution thereby lowering the
266 performance of photo-assisted Fenton reaction, as previously reported (Rivas et al. 2015).

267 The Langmuir-Hinshelwood model that is widely used in heterogeneous catalysis was tested
268 here (Turchi et al. 1990) to describe the oxidation process at the oxide surface. This
269 Langmuir-Hinshelwood model can be expressed as:

$$270 \quad k_{app} = \frac{k_{int} K_s}{1 + K_s C_0} \quad (4)$$

271 and linear expression :

$$272 \quad \frac{1}{k_{app}} = \frac{C_0}{k_{int}} + \frac{1}{k_{int} K_s} \quad (5)$$

273 where k_{app} is the initial pseudo-first-order rate constant (min^{-1}), k_{int} is the intrinsic reaction rate
274 constant ($\mu\text{mol L}^{-1} \text{min}^{-1}$), and K_s is the adsorption constant of FLU over laterite surfaces (L
275 μmol^{-1}). The linear correlations ($r^2 = 0.99$) between $1/k_{app}$ and C_o are good at both pH (3 and
276 6.5), indicating that surface reactions of FLU including sorption and oxidation played a key
277 role in determining the rate of the whole reaction. The values of k_{int} and K_s obtained are 0.51
278 $\mu\text{mol L}^{-1} \text{min}^{-1}$ and 0.12 $\text{L } \mu\text{mol}^{-1}$ at pH 3 and 0.33 $\mu\text{mol L}^{-1} \text{min}^{-1}$ and 0.06 $\text{L } \mu\text{mol}^{-1}$ at pH
279 6.5. The K_s values estimated from L-H model are lower than the constants determined in the
280 absence of oxidant by Langmuir model (1.95 $\text{L } \mu\text{mol}^{-1}$ at pH 3 and 0.37 $\text{L } \mu\text{mol}^{-1}$ at pH 6.5),
281 underscoring competition effects between species at laterite surfaces.

282

283 **3.4. Implication of radical species in the degradation process**

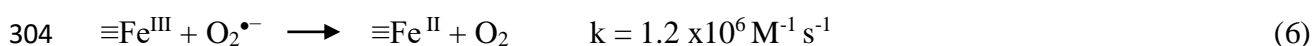
284

285 Different ROS may be formed during heterogeneous photo-Fenton reaction such as $\bullet\text{OH}$
286 and/or $\text{HO}_2\bullet/\text{O}_2^{\bullet-}$ (Martínez et al. 2005; Xue et al. 2009). In order to better understand the
287 process involved in the degradation of FLU, 2-propanol was used as scavenger as it can react
288 with $\bullet\text{OH}$ radical with relatively high reaction rate constant ($k = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Chloroform
289 was also used as the scavenger of $\text{HO}_2\bullet/\text{O}_2^{\bullet-}$ radical due to its relatively high reaction rate
290 constant with hydrated electron ($k = 3.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) and relatively low reaction rate
291 constant with $\bullet\text{OH}$ radical ($k = 7.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (Anbar and Neta, 1967). Because the pKa of
292 $\text{HO}_2\bullet/\text{O}_2^{\bullet-}$ is 4.8, the hydroperoxide anion $\text{HO}_2\bullet$ is the predominant form at pH 3 while the
293 superoxide anion $\text{O}_2^{\bullet-}$ is preponderant at pH 6.5 (Bielski et al. 1985).

294 First, 10 mmol L^{-1} of 2-propanol fully inhibited the FLU degradation (only oxidation is
295 considered here as the total FLU concentration was plotted versus time, Fig. S6), suggesting
296 that the $\bullet\text{OH}$ radical was by far the dominant species in the FLU degradation at pH 3. At pH
297 6.5, 2-propanol did not fully stopped the FLU degradation, while the effect of chloroform is

298 more pronounced than at pH 3, suggesting that hydroxyl radicals still predominantly degrade
299 FLU, but to a lower extent.

300 In the presence of 10 mmol L⁻¹ of chloroform, the percentage of removed FLU fell down from
301 50% in the absence of chloroform to around 37% at pH 6.5, suggesting that O₂^{•-} radicals may
302 play a role in FLU degradation (Fig. S6). O₂^{•-} can promote the formation of [•]OH through the
303 reduction of Fe^{III} to Fe^{II} (Bielski et al. 1985; Lin and Gurol 1998):



305 Nevertheless, the use of 2-propanol at both tested pH led to relatively high inhibition of
306 degradation, confirming that the oxidation of FLU is mainly due to [•]OH radicals.

307

308 **3.5. Effect of co-occurring antibiotic on the FLU degradation**

309 The influence of presence of co-solute on the degradation efficiency of FLU was evaluated
310 with the optimum conditions for laterite loading and oxidant concentration and at two pH
311 values (3 and 6.5). The photo-assisted degradations of FLU ($[k_{\text{FLU}}, \bullet\text{OH}] = 8.26 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at
312 pH 7 (Santoke et al. 2009)) and NOR ($[k_{\text{NOR}}, \bullet\text{OH}] = 6.18 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7 (An et al. 2010))
313 were evaluated in separate system (FLU or NOR) and binary system (an equimolar mixture of
314 FLU and NOR) (Fig.6).

315 Firstly, the degradation of each compound in the mixture decreased with respect to the single
316 system, probably due to competition of compounds for reaction with hydroxyl radicals.

317 As an attempt to better understand the competition effect, the percentage of the hydroxyl
318 radical ([•]OH) reacted with FLU can be estimated using the following equation (Huang et al.
319 2013):

320

$$321 \quad R_{\text{Flu}} = \frac{k_{\bullet\text{OH}, \text{Flu}} [\text{Flu}]_0}{k_{\bullet\text{OH}, \text{Flu}} [\text{Flu}]_0 + k_{\bullet\text{OH}, \text{Nor}} [\text{Nor}]_0 + k_{\bullet\text{OH}, \text{H}_2\text{O}_2} [\text{H}_2\text{O}_2]_0} \quad (7)$$

322

323 Where $[k_{\cdot\text{OH}, \text{FLU}}]$, $[k_{\cdot\text{OH}, \text{NOR}}]$ and $[k_{\cdot\text{OH}, \text{H}_2\text{O}_2}]$ are the second-order rate constants between
324 $\cdot\text{OH}$ and FLU, NOR and hydrogen peroxide. $k_{\cdot\text{OH}, \text{H}_2\text{O}_2} = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Buxton et al. 1988).
325 $[\text{FLU}]_0$, $[\text{NOR}]_0$ and $[\text{H}_2\text{O}_2]_0$ were their initial concentrations. The same equation can be used
326 to determine the percentage of the hydroxyl radical ($\cdot\text{OH}$) reacted with NOR, by replacing
327 $[\text{FLU}]_0$ by $[\text{NOR}]_0$ in the numerator of eq. 12. Since the reaction rate constants of FLU ($[k_{\text{FLU}, \cdot\text{OH}}] = 8.26 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Santoke et al. 2009) and of NOR ($[k_{\text{NOR}, \cdot\text{OH}}] = 6.18 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (An et al. 2010) with the hydroxyl radical are relatively close, 41% and 31% of $\cdot\text{OH}$ reacted
330 with FLU and NOR, respectively. It is worth noting that these reaction rate constants were
331 determined at pH buffered to 7 (i.e. $\text{pK}_{\text{a}1} < \text{pH} < \text{pK}_{\text{a}2}$ for NOR where the zwitterionic form is
332 the predominant species, and $\text{pH} > \text{pK}_{\text{a}}$ for FLU where the anionic form is predominant),
333 which is different from the working pH value (6.5 ± 0.1) in the present study. Nevertheless,
334 we can conclude that the degradation of each compound (FLU or NOR) is not considerably
335 affected by the presence of the other, underscoring potential benefits of the investigated
336 process in the treatment of multi-components contaminated systems.

337

338 **3.6. Stability and reusability of laterite**

339 The reusability of catalyst is a critical parameter, from an economical point of view, for its
340 usage in large scale reactors (Nidheesh 2015). The reusability of laterite has been evaluated in
341 successive oxidation cycles, with the above-mentioned optimum conditions and at two pH
342 conditions (Fig. 7). At the end of the oxidation process, the solid is easily removed from the
343 reactor, washed with ultra-pure water, and dried at 50°C overnight, and then used for next
344 experiment. The degradation using the recovered catalyst showed a slight difference with the
345 first oxidation cycle, suggesting that the catalytic activity kept constant after five cycles of
346 oxidation reaction. The removal rates of FLU were about $6.4 \times 10^{-3} \text{ min}^{-1}$ at pH 3 and $4.4 \times 10^{-3} \text{ min}^{-1}$ at pH 6.5, whereas percentage efficiencies lied at $94 \pm 2\%$ and $70 \pm 2\%$, respectively.

348 The excellent stability of UVA/H₂O₂/Laterite system was then confirmed through TOC
349 measurements at the end of each oxidation cycle. 72 ± 4% of mineralization was achieved at
350 pH 3 and 50 ± 4% at pH 6.5, and this value remains constant even after 5 oxidation cycles.

351 The dissolved iron concentration measurements showed a very low release of Fe from laterite
352 surfaces (less than 2 wt.% of total Fe initially present in laterite). In addition, XRD
353 diffractogram recorded at the end of oxidation reaction was found to be quite similar with that
354 recorded before reaction (Fig. S1). The excellent stability of the catalytic activity could be,
355 therefore, attributed to the very low iron leaching during oxidation cycles and to the structural
356 stability of the solid.

357

358 **4. Conclusion**

359 We have notably demonstrated that laterite can be effectively used for the removal of
360 flumequine under UVA irradiation and at two pH values 3 and 6.5. The photo-assisted Fenton
361 oxidation using laterite as iron source is dependent on H₂O₂ dose, laterite loading and initial
362 concentration of FLU. The degradation rate firstly increased with the dosage of H₂O₂ or with
363 laterite loading, reached an optimum value and then decreased. The occurrence of these
364 optimums values could be explained by the parasite's scavenging reactions and/or light-
365 screening effects. The apparent heterogeneous reaction rate is dominated by the rate of
366 intrinsic surface chemical reactions including sorption and light-induced reduction of Fe^{III},
367 which are crucial to enhance the oxidation reaction. The laterite-promoted degradation of
368 FLU is not dramatically affected by the presence of NOR, which can be co-found in affected
369 environmental systems. The laterite can be re-used for several oxidation cycles without
370 structural changes or deactivation of surface sites. This environmentally friendly remediation
371 technology may appear as a promising way for water treatment in developing countries, using

372 a low cost natural catalyst and solar light for the removal of fluoroquinolone antibiotics from
373 multi-contaminated waters.

374

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379

380 **Appendix A. Supplementary data**

381 Supplementary data associated with this article can be found, in the online version.

382

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Capture Figures

Fig.1. Adsorption isotherms of flumequine (FLU) on laterite at pH 3 and 6.5: $[\text{FLU}]_0 = 19 - 77 \mu\text{mol.L}^{-1}$; $[\text{Laterite}] = 1 \text{ g L}^{-1}$. Solid lines represent the Langmuir model.

Fig.2. Kinetics of flumequine (FLU) removal for various oxidation processes at pH 3 and pH 6.5: $[\text{FLU}]_0 = 77 \mu\text{mol L}^{-1}$; $[\text{H}_2\text{O}_2] = 1 \text{ mmol L}^{-1}$; $[\text{Laterite}] = 1 \text{ g L}^{-1}$; $[\text{FLU}]_{\text{aq}}$ = aqueous (residual) concentration of flumequine. $[\text{FLU}]_{\text{tot}}$ = total concentration of flumequine representing both aqueous (residual) concentration and adsorbed concentration obtained after desorption. Solid lines represent the pseudo-first order model.

Fig.3. Effect of H_2O_2 concentration on flumequine (FLU) removal by heterogeneous photo-Fenton process at pH 3 and pH 6.5: $[\text{FLU}]_0 = 77 \mu\text{mol L}^{-1}$; $[\text{Laterite}] = 1 \text{ g L}^{-1}$; UVA irradiation; reaction time = 420 min.

Fig.4. Effect of laterite dosage on flumequine (FLU) removal by heterogeneous photo-Fenton process at pH 3 and pH 6.5: $[\text{FLU}]_0 = 77 \mu\text{mol L}^{-1}$; UVA irradiation; $[\text{H}_2\text{O}_2] = 4 \text{ mmol L}^{-1}$; reaction time = 420 min.

Fig.5. kinetic rate constants of flumequine (FLU) versus initial concentration of flumequine in heterogeneous photo-Fenton processes at pH 3 and pH 6.5: $[\text{FLU}]_0 = 19 - 77 \mu\text{mol L}^{-1}$; $[\text{laterite}] = 1 \text{ g L}^{-1}$; $[\text{H}_2\text{O}_2] = 4 \text{ mmol L}^{-1}$; UVA irradiation ; reaction time = 420 min.

Fig.6. Total concentration of flumequine (FLU) and norfloxacin (NOR) degraded versus time in single and binary systems in the heterogeneous photo-Fenton process at two pH values (3 and 6.5): $[\text{FLU}]_0 = [\text{NOR}]_0 = 19 \mu\text{mol L}^{-1}$; $[\text{laterite}] = 1 \text{ g L}^{-1}$; $[\text{H}_2\text{O}_2] = 4 \text{ mmol L}^{-1}$; UVA irradiation; reaction time = 300 min.

Fig.7. Reusability cycles of laterite in the heterogeneous photo-Fenton process at pH 3 and pH 6.5: $[\text{FLU}]_0 = 77 \mu\text{mol L}^{-1}$; $[\text{laterite}] = 1 \text{ g L}^{-1}$; $[\text{H}_2\text{O}_2] = 4 \text{ mmol L}^{-1}$; UVA irradiation; reaction time = 420 min. Solid line represents pseudo-first order kinetic model.

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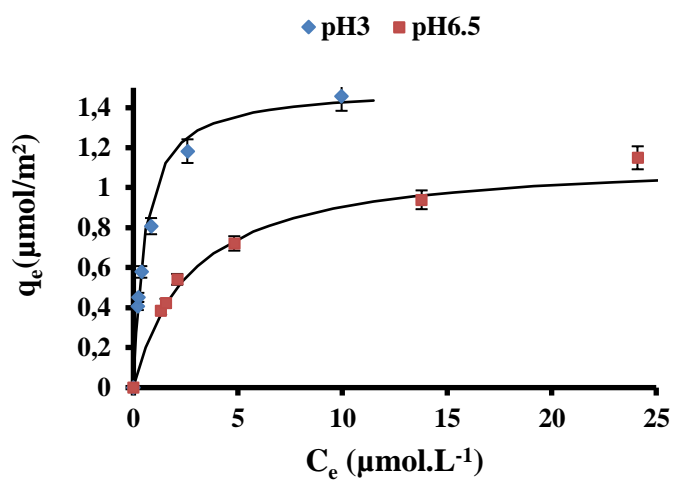


Fig. 1

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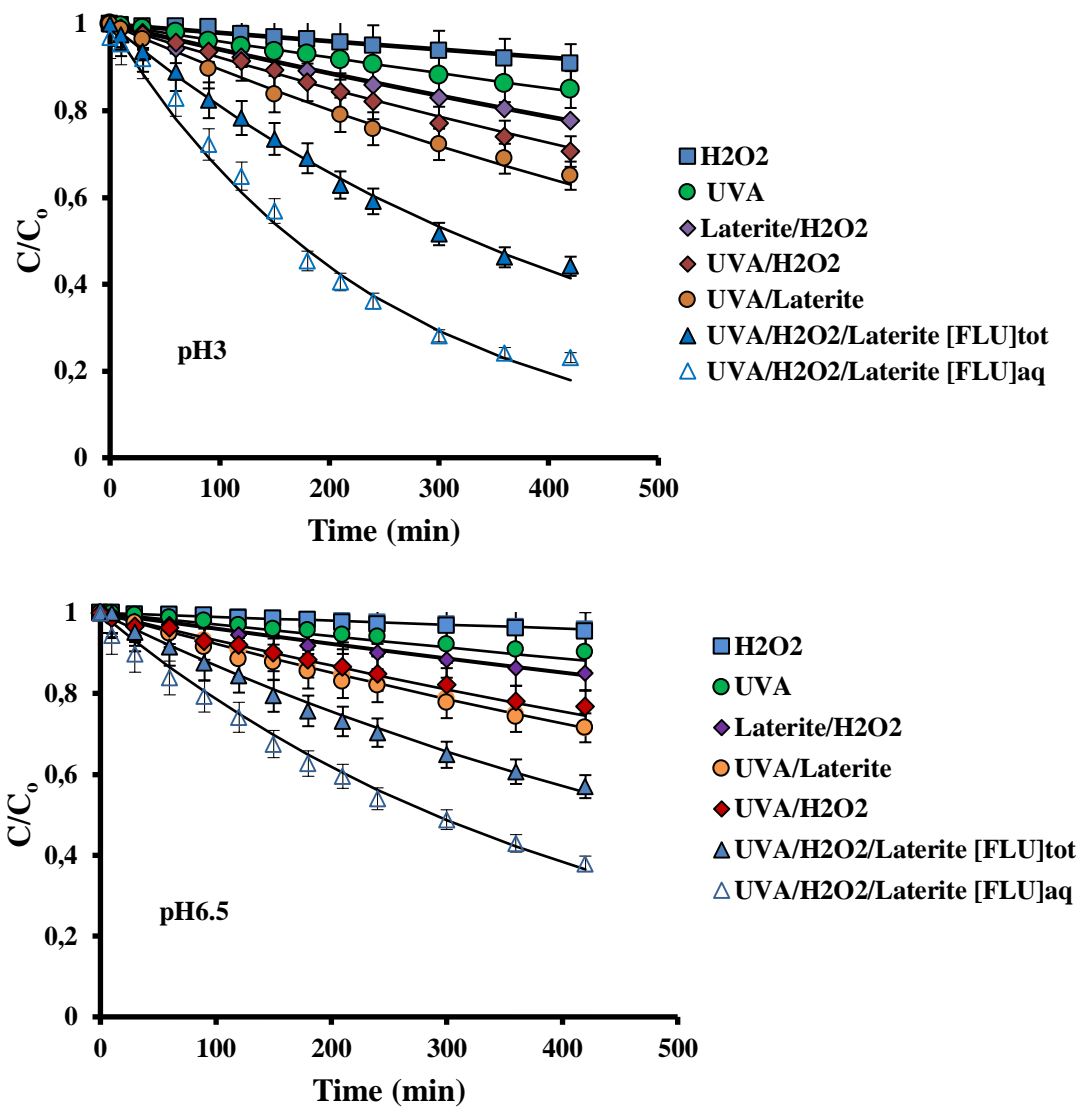


Fig. 2

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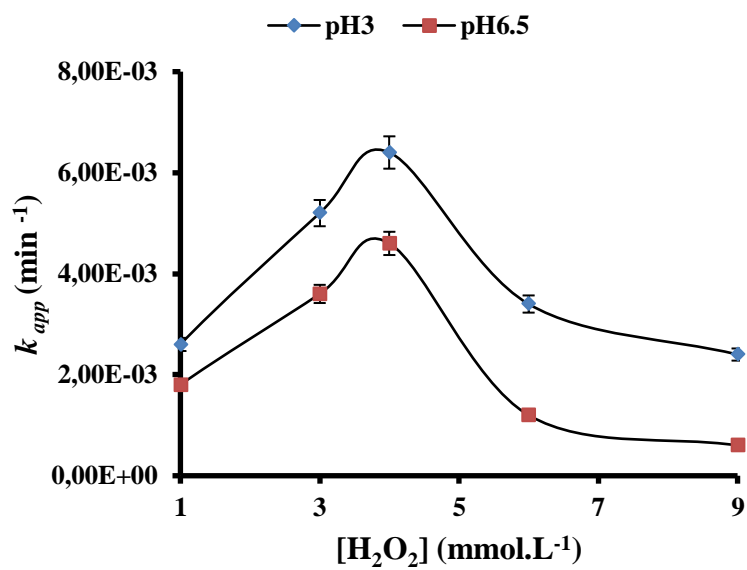
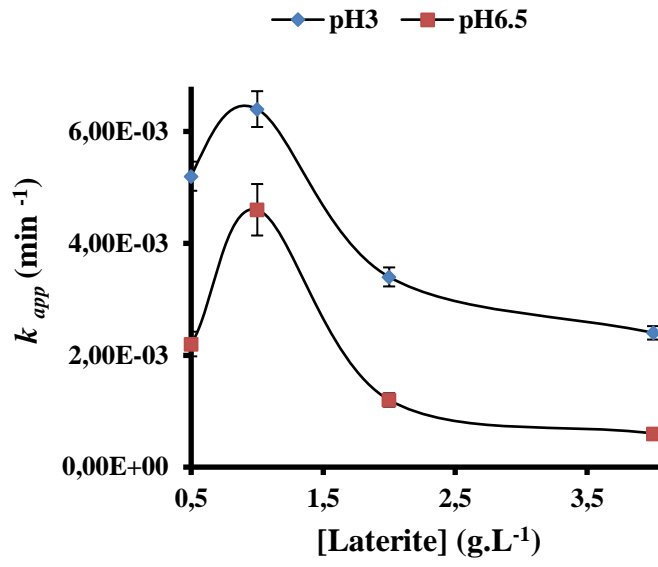


Fig. 3



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Fig. 4

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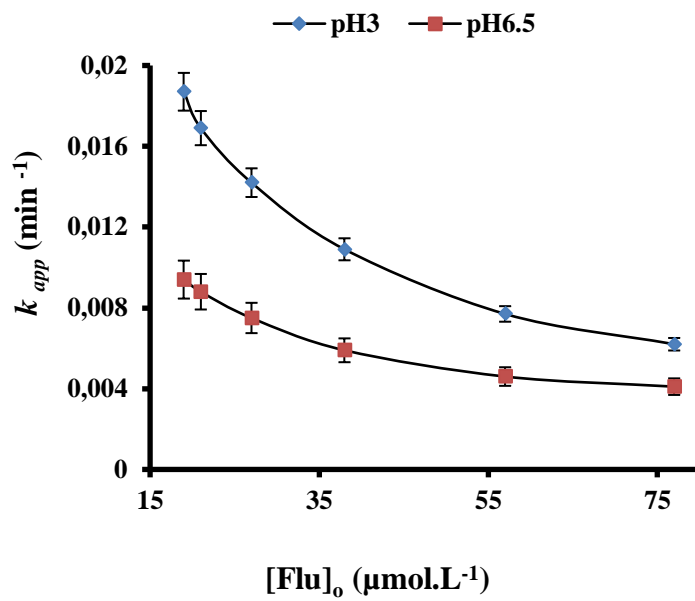


Fig. 5

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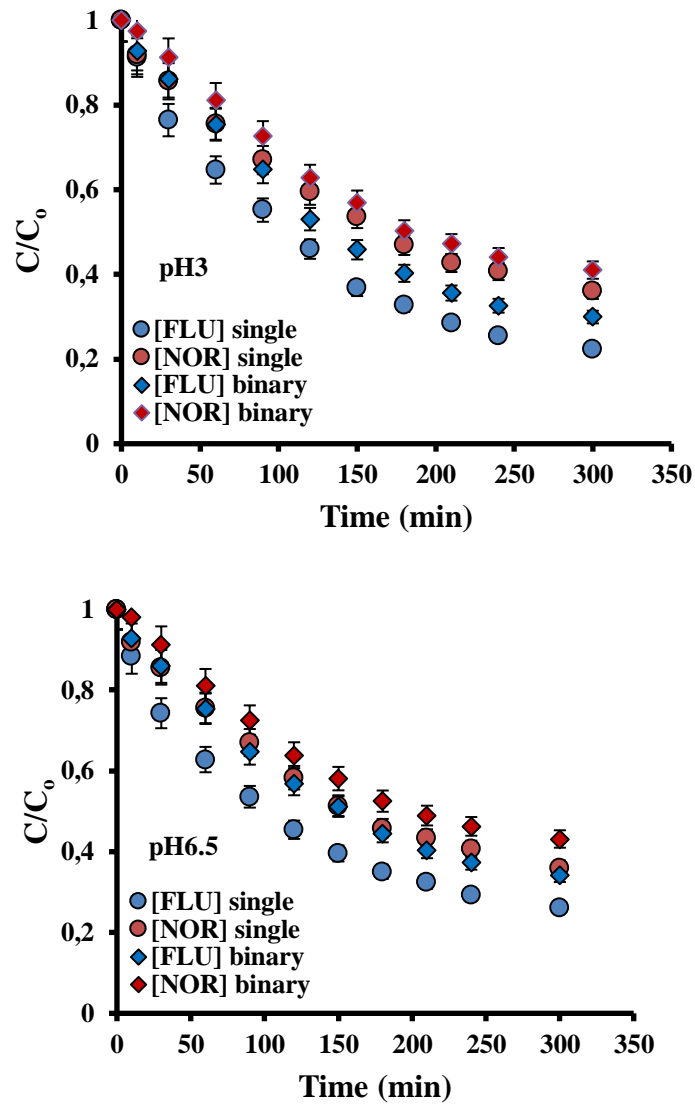


Fig. 6

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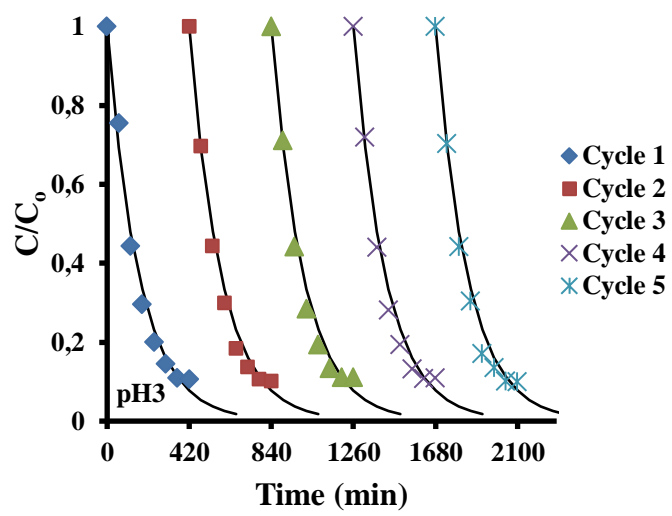
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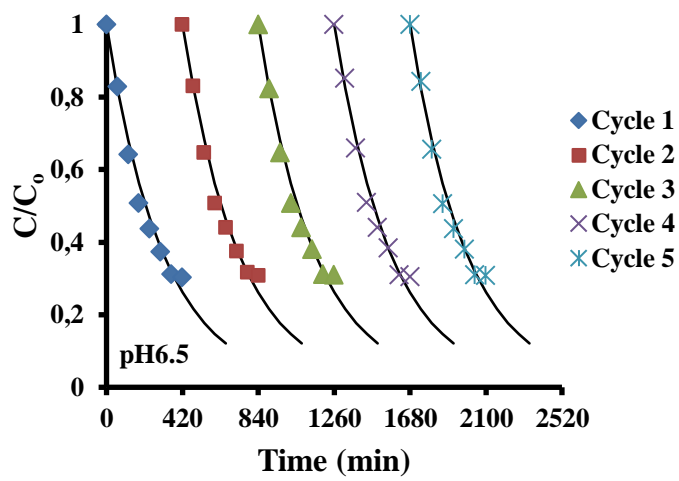
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Fig. 7

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