

1 **Biochar-TiO<sub>2</sub> magnetic nanocomposites for photocatalytic solar-driven**  
2 **removal of antibiotics from aquaculture effluents**

3 **Carla Patrícia Silva<sup>a\*</sup>, Diogo Pereira<sup>a</sup>, Vânia Calisto<sup>a</sup>, Manuel A. Martins<sup>b</sup>, Marta**  
4 **Otero<sup>c</sup>, Valdemar I. Esteves<sup>a</sup>, Diana L.D. Lima<sup>a</sup>**

5 <sup>a</sup>CESAM, Department of Chemistry, University of Aveiro, Campus de Santiago, 3810-  
6 193 Aveiro, Portugal

7 <sup>b</sup>CICECO, Department of Materials and Ceramic Engineering, University of Aveiro,  
8 Campus de Santiago, 3810-193 Aveiro, Portugal

9 <sup>c</sup>CESAM, Department of Environment and Planning, University of Aveiro, Campus de  
10 Santiago, 3810-193 Aveiro, Portugal

11  
12  
13  
14  
15  
16  
17  
18  
19 \_\_\_\_\_  
20 *\*corresponding author*

21 Postal address: CESAM, Department of Chemistry, University of Aveiro, Campus de Santiago,  
22 3810-193 Aveiro, Portugal

23 E-mail address: [patricia.silva@ua.pt](mailto:patricia.silva@ua.pt)

25 **Abstract**

26 Contamination of surrounding waters with antibiotics by aquaculture effluents can be  
27 problematic, due to the possible increase of bacterial resistance, making it crucial the  
28 efficient treatment of those effluents before their release into the environment. In this  
29 work, the application of waste-based magnetic biochar/titanium dioxide (BC/TiO<sub>2</sub>)  
30 composite materials on the photodegradation of two antibiotics widely used in  
31 aquaculture (sulfadiazine (SDZ) and oxolinic acid (OXA)) was assessed. Four materials  
32 were synthesized: BCMag (magnetized BC), BCMag\_TiO<sub>2</sub> (BCMag functionalized with  
33 TiO<sub>2</sub>), BC\_TiO<sub>2</sub>\_MagIn and BC\_TiO<sub>2</sub>\_MagEx (BC functionalized with TiO<sub>2</sub> and  
34 afterwards magnetized by *in-situ* and *ex-situ* approaches, respectively). SDZ half-life time  
35 ( $t_{1/2}$ ) noticeably decreased 3.9 and 3.4 times in presence of BCMag\_TiO<sub>2</sub> and  
36 BC\_TiO<sub>2</sub>\_MagEx, respectively. In the case of OXA, even though differences were not so  
37 substantial, the produced photocatalysts also allowed for a decrease in  $t_{1/2}$  (2.6 and 1.7  
38 times, in presence of BCMag\_TiO<sub>2</sub> and BC\_TiO<sub>2</sub>\_MagEx, respectively). Overall, the  
39 here synthesized BC/TiO<sub>2</sub> magnetic nanocomposites through a circular economy process  
40 are promising photocatalysts for a sustainable solar-driven removal of antibiotics from  
41 aquaculture effluents.

42

43 **Keywords:** *Synthetic photocatalysts, photodegradation, carbonaceous nanocomposites,*  
44 *water treatment, waste valorization.*

45

46

47

## 48        **1. INTRODUCTION**

49        Aquaculture has strongly developed in recent decades and has been considered the  
50        fastest growing food production industry. Powered by governmental and technological  
51        impulsion, this sector is set to increase by further 60-100% over the next 20-30 years.  
52        Like most human food-production activities, aquaculture has been raising several issues  
53        related to environmental welfare and consumer safety. For instance, the increasing of  
54        aquaculture production to give response to the growing demand for fish products that  
55        follows the depletion of natural resources, has led to the wide application of antibiotics  
56        for both prevention and treatment of bacterial diseases (Fedorova et al., 2014; Seoane et  
57        al., 2014). Medicated feeds are the main route of drug administration due to low cost and  
58        easiness of application, but a considerable portion of the administered food may not be  
59        eaten or absorbed by fish, reaching the aquatic environment (Seoane et al., 2014).  
60        Besides, administered pharmaceuticals are not fully metabolized, being excreted in their  
61        original form and released into receiving waters. Antibiotics, such as oxolinic acid (OXA)  
62        and sulfadiazine (SDZ), have been detected in surface waters as a result of their  
63        widespread use in fish farms (Lai and Lin, 2009). Losses of OXA from sparids farmings  
64        to the environment were already estimated to be around 1900 kg/year (Rigos et al., 2004),  
65        while for SDZ, concentrations of 4 ng L<sup>-1</sup> in surface water were related to its use in  
66        freshwater aquaculture facilities (Giang et al., 2015). Moreover, the Frontiers 2017 report  
67        from the United Nations, stated that up to 75 % of antibiotics used in aquaculture may be  
68        lost into the surrounding environment (UNEP, 2017). This massive use of antibiotics,  
69        linked to their discharge into the environment, may lead to the increase of antimicrobial  
70        resistance (AMR), which is considered a major public health problem of the 21<sup>st</sup> century  
71        (UNEP, 2017; WHO, 2020).

72        Photolysis has been shown to be a relevant pathway for the natural attenuation of  
73    aquaculture antibiotics in surface waters (Louros et al., 2020a,b). Thus, the application of  
74    phototreatments using solar radiation could be an interesting and green option for the  
75    removal of antibiotics in aquaculture effluents, not only before their discharge into the  
76    environment but also from recirculating aquaculture systems (RAS). In what concerns  
77    RAS, the use of phototreatments may increase the sustainability of this industry in  
78    conjugation with the water recirculation/reutilization. Phototreatments may allow  
79    substituting pre-existent processes considered either expensive, such as UV treatment, or  
80    harmful, such as ozonation (formation of toxic by-products, such as bromate ( $\text{BrO}_3^-$ ) and  
81    bromoform ( $\text{CHBr}_3$ ), resulting from the reaction between ozone and natural constituents  
82    of salty water aquaculture) (Gonçalves and Gagnon, 2011). However, since low  
83    efficiency may be a drawback, the utilization of synthetic photosensitizers (SPS) may  
84    offer advanced opportunities for the implementation of such phototreatments in the above  
85    referred contexts. Among the most widely used SPS, especially under solar radiation, is  
86    titanium dioxide ( $\text{TiO}_2$ ), as for its availability, high photocatalytic activity, great stability,  
87    non-environmental impact, and cost-effectiveness (Basha et al., 2011; Do et al., 2019).  
88    Novel strategies to improve the practical application of  $\text{TiO}_2$ , include the use of  
89    carbonaceous materials- $\text{TiO}_2$  composites, which have already been used in the removal  
90    of pharmaceuticals from water (e.g. Basha et al., 2011; Briche et al., 2020; Khraisheh et  
91    al., 2013; Lazarotto et al., 2020; Murgolo et al., 2015; Nawaz et al., 2017; Xie et al., 2019;  
92    Zhang et al., 2017). Although the inclusion of magnetic particles in these composites has  
93    already been assessed (Chen et al., 2020), to the best of authors' knowledge, the  
94    application of such materials on the removal of pharmaceuticals has not been evaluated.

95        Carbonaceous- $\text{TiO}_2$  materials present several advantages: (i) have higher  
96    photocatalytic activity relatively to bare  $\text{TiO}_2$ , since the high specific surface area of

97 carbonaceous materials help to harvest the pharmaceuticals and concentrate them close  
98 to the TiO<sub>2</sub> active site; (ii) act as electron scavengers (due to their large electron storage  
99 capacity) as well as sensitizers (providing electrons to TiO<sub>2</sub>); and (iii) reduce the band  
100 gap and extend the absorption band into the lower energy range due to the presence of  
101 carbon-oxygen-titanium linkages in the composite system (Awfa et al., 2018). However,  
102 these carbonaceous materials-TiO<sub>2</sub> composites reported in literature do not present  
103 magnetic properties, which is a major drawback. The magnetization of these composites  
104 can be a feasible solution, essential to improve their after-use separation by simply  
105 applying an external low strength magnetic field. Between carbonaceous materials,  
106 biochar (BC) deserves special attention owing to its low-cost, and stability. Moreover, it  
107 is environmentally friendly, and it can be produced from a wide range of biomass and  
108 industrial wastes (Kwon et al., 2021; Lazarotto et al., 2020; Mian and Liu, 2018). Sludge  
109 from pulp and paper industry is among industrial wastes and its use as raw material to  
110 produce BC has already been shown to be feasible (Calisto et al., 2014; Ferreira et al.,  
111 2017). Indeed, such a production represents an alternative management option for these  
112 residues, in line with the circular economy paradigm, by replacing the end-of-life concept  
113 (where the waste is thought to be discarded, constituting an environmental problem itself)  
114 with upcycling (by adding value to an otherwise end-of-life product).

115 In the above-described context, the main objectives of this work were: (i) the synthesis  
116 and characterization of BC-TiO<sub>2</sub> magnetic composites produced by functionalization of  
117 BC, derived from paper mill sludge, through different magnetization processes; and (ii)  
118 the evaluation of the resulting composites' performance as SPS in order to increase the  
119 photodegradation rate of two antibiotics largely used in aquaculture (sulfadiazine (SDZ)  
120 and OXA). Moreover, this work also aimed to contribute for the development of a

121 sustainable photocatalytic process for antibiotics removal from water, by conjugating  
122 solar radiation and the use of waste-based SPS.

123

## 124 **2. MATERIALS AND METHODS**

### 125 **2.1. Chemicals and solutions**

126 SDZ (> 99%) and OXA (> 98%) were provided from TCI Europe and Fisher  
127 Scientific, respectively. Phosphate buffer stock solution (1 L) was prepared using 0.05  
128 mol of sodium dihydrogen phosphate dihydrate (Fluka, Biochemika,  $\geq 99.5\%$ ) and 0.05  
129 mol of di-sodium hydrogen phosphate dihydrate (Fluka, Biochemika,  $\geq 99\%$ ), which was  
130 diluted to  $0.001 \text{ mol L}^{-1}$  and pH adjusted to 7.3 using hydrochloric acid (NormaPur, 37%).  
131 SDZ stock solution was prepared in ultrapure water and OXA stock solution was prepared  
132 by dissolving the compound in  $0.03 \text{ mol L}^{-1}$  sodium hydroxide solution and sonicated for  
133 60 min. Then, SDZ and OXA working solutions were prepared in  $0.001 \text{ mol L}^{-1}$   
134 phosphate buffer and pH was adjusted to 7.3 using hydrochloric acid (NormaPur, 37%).  
135 Titanium(IV) *n*-butoxide ( $\text{Ti}(\text{O}i\text{Bu})_4$ ; > 99%) was provided by Alfa Aesar, while ethanol  
136 (> 99%) was from Riedel-de-Haën. Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , > 99%)  
137 and ferrous sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , > 99%) were purchased from Chem-  
138 Lab. Potassium hydroxide ( $\geq 86\%$ ) was obtained from LABCHEM. For high-  
139 performance liquid chromatography with a UV-visible detector (HPLC-UV) analysis,  
140 methanol (Fisher Scientific, HPLC grade) and formic acid (Sigma-Aldrich, > 98%) were  
141 used. Ultrapure water was obtained using a purification water system Elga Purelab Flex  
142 4 from Elga (Veolia).

143

144

145

## 146 2.2. Preparation of carbonaceous magnetic nanocomposites

### 147 2.2.1. BC production

148 BC was produced by conventional pyrolysis of primary paper mill sludge, which was  
149 collected from a factory operating with eucalyptus wood (*Eucalyptus globulus*) and kraft  
150 elemental chlorine free production process. Sludge was dried at room temperature  
151 followed by a 24 h period at 105 °C in an oven, and it was then grinded with a blade mill.  
152 The pyrolysis was carried out under nitrogen-controlled atmosphere at 800 °C, for 150  
153 min, according to the procedure described in Calisto et al. (2014). The resulting BC was  
154 washed with 1.2 mol L<sup>-1</sup> HCl, followed by distilled water until the washing leachate  
155 reached neutral pH, allowing to remove ashes generated during pyrolysis and other  
156 inorganic components present in the raw material. Finally, BC was oven-dried at 105 °C  
157 for 24 h, sieved (<180 μm), and stored until use. The BC obtained through the above-  
158 described procedure was used as precursor of the magnetic nanocomposites, as described  
159 in sections 2.2.2 and 2.2.3.

### 161 2.2.2. Magnetization procedure

162 Magnetic nanoparticles were prepared via co-precipitation as described by Pereira et  
163 al. (2021). Briefly, a mixture of Fe<sup>2+</sup> and Fe<sup>3+</sup> salts (FeCl<sub>3</sub>.6H<sub>2</sub>O:FeSO<sub>4</sub>.7H<sub>2</sub>O, 1:3 w/w)  
164 was dissolved in 50 mL of previously deoxygenized distilled water, under N<sub>2</sub> stream, to  
165 which it was added a 0.5 mol L<sup>-1</sup> KOH solution (50 mL) dropwise. The mixture was kept  
166 at 70-80 °C for 1 h under constant mechanical agitation. A black precipitate (magnetic  
167 iron oxides) was magnetically decanted, washed with distilled water until neutral pH and  
168 dried at 40 °C overnight or until completely dry.

169 Magnetization of carbonaceous precursors by co-precipitation can be achieved via  
170 two distinct synthesis routes: *in-situ* or *ex-situ* (Rocha et al., 2020). In this work, magnetic

171 BC (BCM<sub>ag</sub>) was prepared via *in-situ*, while BC/TiO<sub>2</sub> heterostructures (BC\_TiO<sub>2</sub>)  
172 (which synthesis is described in section 2.2.3) were impregnated with magnetic particles  
173 using both *in-situ* (BC\_TiO<sub>2</sub>\_MagIn) and *ex-situ* (BC\_TiO<sub>2</sub>\_MagEx) synthesis routes. In  
174 the *in-situ* procedure, BC or BC\_TiO<sub>2</sub> was added to the iron salt mixture mentioned  
175 above, before the addition of the alkali solution (0.5 mol L<sup>-1</sup> KOH), at 1:6 (*w/w*) mass  
176 ratio in relation to the iron salt content. Alternatively, the *ex-situ* route involved the  
177 suspension of both magnetic nanoparticles and BC\_TiO<sub>2</sub> in deoxygenized water (1:1  
178 *w/w*), under N<sub>2</sub> stream. Subsequently, the pH was adjusted to 5-5.50, which is between  
179 the points of zero charge (PZC) of BC\_TiO<sub>2</sub> (PCZ < 5, determined according to the  
180 procedure described in Pereira et al. (2020) and magnetite (PZC (~6.4-8.0, determined by  
181 Kosmulski (2016))), thus promoting surface attraction.

182 Finally, for all materials, magnetic separation from solution was performed using a  
183 neodymium rod-shaped magnet (1 cm diameter; 4 cm height; 1.26-1.29 T).

184

### 185 **2.2.3. Synthesis of BC/TiO<sub>2</sub> heterostructures**

186 BC/TiO<sub>2</sub> and magnetic BC/TiO<sub>2</sub> heterostructures were obtained following a  
187 solvothermal synthesis, adapted from Peñas-Garzón et al. (2019). BC or BCM<sub>ag</sub> (58 mg)  
188 were suspended in 45 mL of ethanol for 5 min, at room temperature (solution A). At the  
189 same time, solution B was prepared by adding 1 mL of Ti(OBu)<sub>4</sub> (Ti precursor) to 15 mL  
190 of ethanol, which was then stirred for 5 min. Then, solution B was added dropwise, under  
191 continuous stirring, to solution A. To promote the hydrolysis of Ti(OBu)<sub>4</sub>, a third  
192 solution, containing 3 mL of ultrapure water and 15 mL of ethanol, was added dropwise  
193 to the previous mixture, and stirred for 5 min. The final solution was transferred to a  
194 Teflon-lined stainless-steel autoclave and heated for 3 h at 160 °C. After this procedure,  
195 the mixture was centrifuged for 10 min at 5500 rpm. The supernatant was discarded and



196 the solid was washed 3 times with water and with ethanol. Finally, the resulting material  
197 was dried at 60 °C overnight. BCMag\_TiO<sub>2</sub> was stored until use in a desiccator, while  
198 BC\_TiO<sub>2</sub> was subjected to the magnetization procedure previously described (section  
199 2.2.2) and stored until use in a desiccator.

200

### 201 **2.3. Characterization of carbonaceous magnetic nanocomposites**

202 Scanning electron microscopy (SEM) images were obtained using a scanning  
203 electron microscope, analytical and high resolution Schottky emission (HR-SEM-SE),  
204 Hitachi model SU-70, equipped with energy dispersive X-ray microanalysis (EDS),  
205 Bruker model Quantax 400.

206 X-ray diffraction (XRD), conducted to evaluate the structural properties of the  
207 synthesized powders, was acquired using a Malvern Panalytical, Epyrean  
208 diffractometer with the Cu (K $\alpha$ ) radiation in a  $2\theta$  range of 8–70°.

209 The magnetization measurements were carried out in a vibrating sample  
210 magnetometer (VSM EV9), with an applied magnetic field to a maximum of 22 kOe. By  
211 plotting the magnetic moment as a function of the applied magnetic field, it was possible  
212 to determine the saturation magnetization ( $M_s$ ) of each synthesised nanocomposite,  
213 dividing the *plateau* found for the magnetic moment by the mass of material. The sample  
214 (*ca.* 10 mg) was encapsulated in an acrylic cylindrical vessel (5.85 mm diameter  $\times$  2.60  
215 mm height), which was coupled to the linear motor of the VSM EV9 instrument, centred  
216 between the two polar heads of the electromagnet used to provide the magnetic field.  
217 Prior to the analysis, the instrument was calibrated with a disk of pure nickel and applying  
218 a magnetic field of *ca.* 1 Oe and with dispersion on the magnetic moment inferior to 0.5%.

219 The determination of the TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> percentages in the synthesised materials was  
220 determined by wavelength-dispersive X-ray fluorescence (WDXRF). The XRF analysis

221 was performed using an Axios, MalvernPanalytical spectrometer, under inert atmosphere  
222 (He) and applying a maximum voltage of 36, 50 and 60 kV, and a maximum current of  
223 60, 72 and 100 mA.

224

#### 225 **2.4. Chromatographic and dissolved organic carbon analyses**

226 Chromatographic analysis of SDZ and OXA was performed using a Water Alliance  
227 2695 Separation Module equipped with a Waters 2487 Dual Absorbance detector.  
228 Samples (20  $\mu\text{L}$ ) were injected in an ACE<sup>®</sup> C18 column-PFP (150 mm  $\times$  4.6 mm i.d. with  
229 5  $\mu\text{m}$  particle size) connected to a 4.6 mm i.d. ACE<sup>®</sup> 5 C18 guard, which was maintained  
230 at 25  $^{\circ}\text{C}$ . The mobile phase consisted of methanol:0.1% formic acid, 20:80 (v/v) or 45:55  
231 (v/v), for the analysis of SDZ and OXA, respectively. A flow rate of 0.9  $\text{mL min}^{-1}$  was  
232 used, and the detection of both compounds was performed at 270 nm. Before use as  
233 mobile phase, methanol and 0.1% formic acid aqueous solutions were filtered through a  
234 0.2  $\mu\text{m}$  polyamide membrane filter (Whatman).

235 Mineralization of OXA and SDZ during photodegradation was determined by  
236 measuring the remaining dissolved organic carbon (DOC) in solution along irradiation.  
237 For the analysis of DOC, a Total Organic Carbon analyser, TOC-V<sub>CPH</sub>, from Shimadzu  
238 was used. Previously to the analysis, samples were acidified with 2% (v/v) of HCl 2 mol  
239  $\text{L}^{-1}$ . Calibration curve was performed using standard solutions of potassium hydrogen  
240 phthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ ) (diluting proper amounts of the 1000  $\text{mg L}^{-1}$   $\text{KHC}_8\text{H}_4\text{O}_4$  stock  
241 solution in ultrapure water) with concentrations ranging from 0.0 to 10.0  $\text{mg L}^{-1}$   
242  $\text{KHC}_8\text{H}_4\text{O}_4$ . The coefficient of determination ( $R^2$ ) and limit of detection (LOD) for the  
243 obtained calibration curve were 0.9984 and 0.613  $\text{mg L}^{-1}$  C, respectively. Daily and prior  
244 to the analysis of the samples, the calibration curve stability was evaluated, using a newly  
245 prepared standard solution of 5.0  $\text{mg L}^{-1}$   $\text{KHC}_8\text{H}_4\text{O}_4$ .

## 2.5. Photolysis experiments

Experiments on the photodegradation of SDZ and OXA in the absence or presence of the synthesized nanocomposites were carried out under simulated solar irradiation using a Solarbox 1500 (Co.fo.me.gra, Italy). The irradiation device contained an arc xenon lamp (1500 W) and outdoor UV filters that limited the transmission of light with wavelengths below 290 nm. The irradiance of the lamp was  $55 \text{ W m}^{-2}$  (290-400 nm), which was kept constant throughout all the experiments. Likewise, the device was refrigerated by an air-cooled system to keep a constant temperature inside. To monitor the irradiance level and temperature, a multimeter (Co.fo.me.gra, Italy) equipped with a UV 290-400 nm large band sensor and a black standard temperature sensor, were used. Furthermore, a parabolic reflection system guaranteed the uniformity of the irradiation inside the chamber.

Solutions of either SDZ or OXA, in the absence or presence of any of the synthesized materials, were transferred into quartz tubes (1.8 cm internal diameter  $\times$  20 cm height). To hold the quartz tubes suspended inside the irradiation chamber, a home-made metallic holder was used, which allowed for homogeneous irradiation. For each set of experiments, four tubes were introduced into the Solarbox: three of them were exposed to radiation and one was covered with several layers of aluminum foil to protect it from light (dark control). The dark control was kept inside the Solarbox during the same time as the irradiated solutions and was used to determine adsorption of the corresponding antibiotic onto the nanocomposite under study.

Photodegradation of SDZ and OXA was studied in the absence or presence of the different synthesized nanocomposites. Initially, solutions of SDZ ( $5 \text{ mg L}^{-1}$ ) and OXA ( $10 \text{ mg L}^{-1}$ ) were irradiated in absence of any material for 14 h and 1 h, respectively. Then, solutions with the same concentrations were irradiated in presence of 25, 50 and

271 100 mg L<sup>-1</sup> of each nanocomposite for the same time, as preliminary tests to find out their  
272 respective efficiencies.

273 Next, SDZ (5 mg L<sup>-1</sup>) and OXA (10 mg L<sup>-1</sup>) solutions were irradiated for 5 h and 15  
274 min, respectively, in absence of any material and in presence of the two selected most  
275 efficient SPS (BCMag\_TiO<sub>2</sub> and BC\_TiO<sub>2</sub>\_MagEx) at higher concentrations (100, 250  
276 and 500 mg L<sup>-1</sup>). After the corresponding irradiation time, photodegradation was  
277 determined by comparing the antibiotic concentration in the irradiated solution (*C*) with  
278 the concentration in the corresponding dark control (*C*<sub>0</sub>). Adsorption onto each SPS was  
279 determined by comparing initial SDZ and OXA concentrations (*C*<sub>*i*</sub>) before the addition  
280 of the SPS with *C*<sub>0</sub>.

281 Finally, SDZ and OXA photodegradation kinetic experiments were performed using  
282 10 mg L<sup>-1</sup> (*C*<sub>*i*</sub>) solutions in the absence and presence of the two most efficient SPS at the  
283 selected concentration from results of the previous set of experiments. For each irradiation  
284 time, aliquots from the three irradiated tubes and from the dark control were collected and  
285 analysed for the concentration of the corresponding antibiotic and DOC.

286

### 287 **3. RESULTS AND DISCUSSION**

#### 288 **3.1. Characterization of carbonaceous magnetic nanocomposites**

289 The SEM images of BCMag, BCMag\_TiO<sub>2</sub>, BC\_TiO<sub>2</sub>\_MagIn and  
290 BC\_TiO<sub>2</sub>\_MagEx are depicted in Figure S1, in Supplementary Material (SM).

291 Porous structure of the different composites was revealed in the nanoscale image.  
292 BCMag appeared as micrometer size granules (1-10 μm) with smaller spherical-like  
293 morphology particles on their surface (less than 100 nm). Smoother granules with *ca.* 500  
294 nm were observed when the Ti precursor was added in the preparation, namely in the case  
295 of BCMag\_TiO<sub>2</sub>, which can be attributed to the TiO<sub>2</sub> coating. Materials in which the

296 magnetization was performed after the TiO<sub>2</sub> incorporation, viz. BC\_TiO<sub>2</sub>\_MagIn and  
297 BC\_TiO<sub>2</sub>\_MagEx, presented a rougher surface than BCMag\_TiO<sub>2</sub>, in which TiO<sub>2</sub> was  
298 introduced after the magnetization procedure. The roughness of BC\_TiO<sub>2</sub>\_MagIn and  
299 BC\_TiO<sub>2</sub>\_MagEx could be attributed to the iron nanoparticles loaded on the TiO<sub>2</sub> surface.  
300 Indeed, the relatively high iron content of BC\_TiO<sub>2</sub>\_MagIn e BC\_TiO<sub>2</sub>\_MagEx, as  
301 compared to BCMag\_TiO<sub>2</sub>, was confirmed by EDS analysis, which results are presented  
302 in Table S1.

303 The higher iron content and  $M_s$  of BC\_TiO<sub>2</sub>\_MagIn and BC\_TiO<sub>2</sub>\_MagEx, in which  
304 TiO<sub>2</sub> was incorporated before magnetization, as compared with BCMag\_TiO<sub>2</sub> was further  
305 confirmed by WDXRF and VSM analyses, which results are presented in Table S2.  
306 Compared to the materials containing TiO<sub>2</sub>, BCMag presented a higher iron content, as  
307 well as a higher  $M_s$ . Moreover, comparing BCMag and BCMag\_TiO<sub>2</sub>, which  
308 magnetization was *in-situ* in both cases, it may be concluded that the incorporation of  
309 TiO<sub>2</sub> in BCMag originated the loss of iron content, as well as a decrease in  $M_s$ . Anyway,  
310 complete and fast magnetic separation from aqueous medium was verified for the three  
311 SPS here produced.

312 XRD analysis (Figure S2, in SM) showed that BCMag consisted of iron oxides  
313 matching magnetite main reflections at 30.16 (220); 35.53 (311); 37.29 (222); 43.27  
314 (400); 53.60 (422); 57.11 (511); 62.69 (440) (JCPDS card No. 89-691). The incorporation  
315 of TiO<sub>2</sub> in BCMag\_TiO<sub>2</sub> was in the form of anatase, as it matched the main crystalline  
316 anatase reflections at 25.30 (101); 37.90 (004); 48.12 (200); 55.34 (211) (JCPDS card no.  
317 21-1272), clearly observed along with the peaks from magnetite phase. The contributions  
318 from the anatase phase were also observed for BC\_TiO<sub>2</sub>\_MagIn and BC\_TiO<sub>2</sub>\_MagEx,  
319 in smaller amounts when compared with BCMag\_TiO<sub>2</sub>, which confirmed the  
320 quantification of the phases as determined by WDXRF (Table S2).

## 3.2. OXA and SDZ photolysis

### 3.2.1. Evaluation of the carbonaceous magnetic nanocomposites' performance

The performance of the four produced materials was evaluated by studying the effect of their presence on SDZ and OXA photodegradation. Figure 1 presents the removal percentage for SDZ and OXA in absence and presence of these nanocomposites at different concentrations. As it may be seen, the presence of all of them increased the removal percentage of both antibiotics as compared with their absence. However, in the case of BCMag, its presence increased the antibiotics overall removal percentage (especially for SDZ, from 50 to 69% for 25 and 100 mg L<sup>-1</sup> BCMag, respectively) but not their photodegradation. Therefore, the antibiotics removal increase was assigned exclusively to their adsorption onto BCMag. Furthermore, the adsorption percentage of both antibiotics increased with BCMag concentration, reaching 33% for SDZ and 16% for OXA. The materials with TiO<sub>2</sub> onto BC surface caused the increase of the antibiotics' photodegradation while adsorptive removal onto these SPS was very small or negligible. This might be due to the blockage of the BC adsorption sites and/or occupation of pore space by Ti nanoparticles so reducing the adsorption capacity of these materials. For BCMag\_TiO<sub>2</sub> and BC\_TiO<sub>2</sub>\_MagEx, the increase of SPS concentration increased the photodegradation removal percentage of both antibiotics. Differently, for BC\_TiO<sub>2</sub>\_MagIn, there was no obvious effect of the SPS concentration and, particularly for OXA, even a photodegradation decrease was observed.

From the four nanocomposites produced and concentrations tested, the highest removal percentages were observed for 100 mg L<sup>-1</sup> BCMag\_TiO<sub>2</sub>, with a removal assigned to photodegradation of 87% for SDZ and 98% for OXA, followed by 100 mg L<sup>-1</sup> BC\_TiO<sub>2</sub>\_MagEx, with 76% for SDZ and 69% for OXA. These results may be explained

346 by the larger TiO<sub>2</sub> content of BCMag\_TiO<sub>2</sub>, followed by BC\_TiO<sub>2</sub>\_MagEx, as  
347 demonstrated by WDXRF analysis (Table S2).

348 *Figure 1*

349 Since for BCMag\_TiO<sub>2</sub> and BC\_TiO<sub>2</sub>\_MagEx an increase in the SPS concentration  
350 originated an increase in the photodegradation of both SDZ and OXA, higher  
351 concentrations were tested to verify if this increase could be even higher and compensate  
352 the materials expenditure and associated economic costs. The obtained results, presented  
353 in Figure 2, demonstrated that for SDZ, the increase in the BCMag\_TiO<sub>2</sub> concentration  
354 did not cause a significant increase of photodegradation percentage. Meanwhile, the  
355 increase in the BC\_TiO<sub>2</sub>\_MagEx concentration resulted in a slight increase in SDZ  
356 removal, not only by photodegradation but also by adsorption. For OXA, the removal  
357 percentage slightly increased with the concentration rise from 100 to 250 mg L<sup>-1</sup> for both  
358 SPS, and also from 250 to 500 mg L<sup>-1</sup> for BC\_TiO<sub>2</sub>\_MagEx; however, such enlargements  
359 were mainly due to the increase of the adsorption percentage.

360 *Figure 2*

361 In view of results shown in Figure 2 and considering that increasing the concentration  
362 of the selected SPS did not result in a proportional removal increase for any antibiotic,  
363 kinetic studies next carried out were done at a concentration of 100 mg L<sup>-1</sup> of either  
364 BCMag\_TiO<sub>2</sub> or BC\_TiO<sub>2</sub>\_MagEx.

365

### 366 **3.2.2. Photocatalytic kinetic studies**

367 Kinetic experimental results on the photodegradation of SDZ and OXA throughout  
368 time, in the absence and presence of 100 mg L<sup>-1</sup> of BCMag\_TiO<sub>2</sub> or BC\_TiO<sub>2</sub>\_MagEx,  
369 together with the corresponding fittings to the pseudo-first order equation  $C/C_0 = e^{-kt}$  (in

370 which  $k$  is the rate constant ( $\text{h}^{-1}$ ),  $t$  is time, and  $C$  and  $C_0$  are the concentration of the  
371 antibiotic at a given irradiation time and the concentration in the corresponding dark  
372 control, respectively) are presented in Figure 3. Also, data on  $k$ , determination coefficient  
373 ( $R^2$ ) and half-life time ( $t_{1/2}$  (h); calculated as  $\ln(2)/k$ ), obtained for SDZ and OXA in  
374 presence and absence of SPS are presented on Table 1.

375 *Figure 3*

376 Figure 3 clearly evidences the slower photodegradation of either SDZ or OXA  
377 in the absence of any SPS. In the case of SDZ, both BCMag\_TiO<sub>2</sub> and BC\_TiO<sub>2</sub>\_MagEx  
378 accelerate photodegradation in a very similar way, while BCMag\_TiO<sub>2</sub> was more  
379 efficient than BC\_TiO<sub>2</sub>\_MagEx in the case of OXA. Nonetheless, for both antibiotics,  
380 kinetic experimental results were adequately described by the pseudo-first order equation  
381 either in the absence or in the presence of the selected SPS.

382 *Table 1*

383 Results in Table 1 confirm the increase in the antibiotics' photodegradation rate in  
384 the presence of either BCMag\_TiO<sub>2</sub> or BC\_TiO<sub>2</sub>\_MagEx and that kinetic experimental  
385 results fitted the pseudo-first order equation in all cases ( $R^2 \geq 0.99$ ). For SDZ,  $k$  increased  
386 from  $0.062 \pm 0.003 \text{ h}^{-1}$  in absence of SPS to  $0.236 \pm 0.008 \text{ h}^{-1}$  in presence of BCMag\_TiO<sub>2</sub>  
387 and  $0.213 \pm 0.007 \text{ h}^{-1}$  in presence of BC\_TiO<sub>2</sub>\_MagEx. Corroborating results in Figure  
388 3,  $k$  obtained for SDZ in presence of BCMag\_TiO<sub>2</sub> and BC\_TiO<sub>2</sub>\_MagEx were only  
389 slightly different. In what concerns  $t_{1/2}$ , a considerable decrease was observed from  $11.2$   
390  $\pm 0.5 \text{ h}$  in absence of SPS to  $2.9 \pm 0.1 \text{ h}$  in presence of BCMag\_TiO<sub>2</sub> and  $3.3 \pm 0.1 \text{ h}$  in  
391 presence of BC\_TiO<sub>2</sub>\_MagEx.

392 For OXA, an increase of  $k$  was also observed for both SPS. However, better results  
393 were obtained using BCMag\_TiO<sub>2</sub> with an increase from  $0.57 \pm 0.04 \text{ h}^{-1}$  in absence of  
394 SPS to  $1.51 \pm 0.03 \text{ h}^{-1}$  in presence of that SPS. Regarding  $t_{1/2}$ , although the decrease was



395 not as noticeable as for SDZ, it was also observed for OXA in presence of both SPS:  $1.21$   
396  $\pm 0.08$  h in absence of SPS decreasing to  $0.71 \pm 0.03$  h in presence of BC\_TiO<sub>2</sub>\_MagEx  
397 and to  $0.46 \pm 0.01$  h in presence of BCMag\_TiO<sub>2</sub>. Still, comparing to SDZ,  $t_{1/2}$  for OXA  
398 were all quite shorter.

399 Ideally, full mineralization of the target antibiotics, which means their complete  
400 conversion into CO<sub>2</sub> and H<sub>2</sub>O, would be the final goal of a phototreatment. Thus,  
401 mineralization along the photocatalytic degradation of OXA and SDZ was followed by  
402 measuring DOC. Figure 4 presents results on the percentage of SDZ mineralization at  
403 each of the irradiation times in the kinetic experiment, as shown in Figure 3. For this  
404 antibiotic and in absence of SPS, it was possible to observe  $13.1 \pm 0.2$  % of mineralization  
405 after 2 h of irradiation; however, in presence of BCMag\_TiO<sub>2</sub>, mineralization was  $27 \pm 2$   
406 %, while for BC\_TiO<sub>2</sub>\_MagEx no increase in the mineralization was observed for such a  
407 short irradiation time. Mineralization of SDZ in absence of SPS increased very slightly  
408 along irradiation time and, after 32 h, only  $20.3 \pm 0.4$  % of SDZ was mineralized. For the  
409 same time, but in presence of SPS, a significant increase in the mineralization percentage  
410 was observed: for BCMag\_TiO<sub>2</sub>, the mineralization reached  $70 \pm 2$  %, while for  
411 BC\_TiO<sub>2</sub>\_MagEx, a mineralization of  $58 \pm 4$  % was observed. The obtained  
412 mineralization percentages are similar to values reported in literature, also for the  
413 degradation of SDZ promoted by a magnetic photocatalyst (Dhiman et al., 2019).

414

415

#### *Figure 4*

416 For OXA, no mineralization was observed during the irradiation time used to follow  
417 the photodegradation kinetics (4 h, as displayed in Figure 3), not even in presence of SPS  
418 (results not shown). Therefore, a correspondence between OXA mineralization  
419 percentage and the photodegradation rate was not verified. In fact, although OXA

420 photodegradation kinetics was quite faster than that of SDZ, its mineralization was much  
421 lower. When irradiation was extended until the longest time used for SDZ, namely 32 h,  
422 no OXA mineralization was observed in absence of SPS (while SDZ mineralized  $20.3 \pm$   
423  $0.4 \%$ ) and mineralization percentages of  $65 \pm 1 \%$  using BCMag\_TiO<sub>2</sub> and of  $44 \pm 1 \%$   
424 using BC\_TiO<sub>2</sub>\_MagEx were attained (compared to  $70 \pm 2\%$  and  $58 \pm 4 \%$ , respectively,  
425 for SDZ). Thus, while no OXA mineralization was verified in the absence of SPS and  
426 even under longer irradiation times, the use of here produced nanocomposites allowed for  
427 a significant increase in mineralization. Still, mineralization results obtained for OXA  
428 contrast with the relatively fast photocatalytic degradation of this antibiotic (Figure 3).  
429 Mineralization not going along with the photodegradation was also observed by  
430 Belhouchet et al. (2019) for tetracycline using a calcite/TiO<sub>2</sub> photocatalyst. This was  
431 related with the possibility of antibiotic molecules degrading along irradiation into small  
432 intermediate metabolites of lower molecular weight (Belhouchet et al., 2019). Overall,  
433 obtained results showed that either BCMag\_TiO<sub>2</sub> or BC\_TiO<sub>2</sub>\_MagEx allowed for a  
434 significant acceleration of SDZ and OXA photodegradation, which demonstrate that these  
435 nanocomposites are promising SPS for application in the solar driven removal of  
436 aquaculture antibiotics from water. However, in the case of OXA, such photodegradation  
437 was not accompanied by equivalent mineralization, which points to the generation of  
438 intermediates during irradiation. Then, a main question is if these intermediates retain the  
439 antibacterial activity of the parent compound. Determination of photoproducts, their  
440 toxicity and antibacterial activity will be the aim of future work, together with the  
441 assessment of photodegradation mechanism.

442 To the best of authors' knowledge there are no results in literature on the application  
443 of BC-TiO<sub>2</sub> magnetic nanocomposites on the photocatalysis of OXA and SDZ under  
444 simulated solar irradiation. However, some studies on the photocatalysed degradation of

445 these antibiotics performed with other systems may be found. For instance, Naciri et al.  
446 (2020) studied the degradation of SDZ by UV light and  $Zn_3(PO_4)_2/BiPO_4$  composites,  
447 concluding that the complete degradation of the antibiotic is accomplished for only 240  
448 min. Authors also studied the mineralization concluding that the mineralization power of  
449 the composite was considerably greater than that of the components alone (3 times greater  
450 than that of  $Zn_3(PO_4)_2$  and 1.5 greater than that of  $BiPO_4$ ). As for OXA, Giraldo et al.  
451 (2010) used  $TiO_2$  merely in suspension, results indicating that 30 min were sufficient to  
452 eliminate both the antibiotic and the antimicrobial activity. On the other hand, Gaeta et  
453 al. (2020) used different porphyrins to functionalize  $TiO_2$  nanomaterials, with results  
454 showing that none of the systems used was better than  $TiO_2$  alone, for which the increase  
455 in photodegradation in comparison with absence of any kind of material was evident.  
456 Likewise, studies on the utilization of  $TiO_2$ - or BC- $TiO_2$ -based nanomaterials (non-  
457 magnetic) for the removal of antibiotics (not including OXA or SDZ) may be found in  
458 literature (Do et al, 2019; Zhang et al., 2017). Results show that these materials degraded  
459 the antibiotics fast (most antibiotics were completely removed after 20 min under  
460 irradiation) (Zhang et al., 2017) and with higher removal efficiency than the pure  $TiO_2$   
461 powder under UV light irradiation (Do et al., 2019).

462 Overall, even though the comparison between this work and others in literature  
463 cannot be directly performed since conditions and systems are different, it may be stated  
464 that the SPS herein produced and applied favourably compare with other options. Also,  
465 it is important to highlight that the magnetization feature is a very important achievement  
466 of this work's composites, which constitute an easy way to recover the material after  
467 treatment.

468

469

#### 4. CONCLUSIONS

Four different carbonaceous magnetic nanocomposites (BCMag (magnetized BC), BCMag\_TiO<sub>2</sub> (BCMag functionalized with TiO<sub>2</sub>), BC\_TiO<sub>2</sub>\_MagIn and BC\_TiO<sub>2</sub>\_MagEx (BC functionalized with TiO<sub>2</sub> and afterwards magnetized by *in-situ* and *ex-situ* approaches, respectively)) were successfully produced in this work using biochar (BC) produced from paper mill sludge. The characterization of these materials pointed to large differences on their respective TiO<sub>2</sub> and iron contents and photodegradation results demonstrated that all of them improved the removal percentage of the aquaculture antibiotics under study, *viz.* OXA and SDZ. BCMag\_TiO<sub>2</sub> and the BC\_TiO<sub>2</sub>\_MagEx were the materials that allowed for a larger photodegradation increase for both antibiotics and therefore were selected for kinetic photocatalytic experiments. Under the presence of these materials, the  $t_{1/2}$  were 3-4 times shorter for SDZ and around 2 times shorter for OXA than in absence of the materials. However, no correlation was observed between photodegradation kinetics and mineralization rate in the case of OXA. Indeed, although OXA displayed a much faster photodegradation than SDZ, its mineralization rate was much slower and only possible in presence of SPS. Globally, the novel BC-TiO<sub>2</sub> magnetic nanocomposites produced in this work demonstrated high potential for application in the photocatalytic removal of antibiotics from aquaculture effluents. Moreover, the synthesis and subsequent application of these nanocomposite materials offers a variety of benefits that include sustainability, cost lowering and the fulfilment of the circular economy paradigm.

494 **5. ACKNOWLEDGMENTS**

495 This work was funded by FEDER through CENTRO 2020 and by national funds  
496 through Fundação para a Ciência e a Tecnologia, I.P. (FCT) within the research project  
497 REM-AQUA (PTDC/ASP-PES/29021/2017). Also, this work is a contribution to the  
498 project WasteMAC (POCI-01-0145-FEDER-028598) funded by FCT, through national  
499 funds, and the co-funding by FEDER, within the PT2020 Partnership Agreement and  
500 Compete 2020. Diana Lima was funded by national funds (OE), through FCT, in the  
501 scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of  
502 the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19. Marta Otero  
503 and Diogo Pereira thank support by FCT Investigator Program (IF/00314/2015). Vânia  
504 Calisto is also thankful to FCT for the Scientific Employment Stimulus support  
505 (CEECIND/00007/2017). Thanks are due, for the financial support to CESAM  
506 (UIDB/50017/2020+UIDP/50017/2020), to FCT/MCTES through national funds.

507

508 **REFERENCES**

509 Awfa, D., Ateia, M., Fujii, M, Johnson, M.S. (2018). Photodegradation of  
510 pharmaceuticals and personal care products in water treatment using carbonaceous-  
511 TiO<sub>2</sub> composites: A critical review of recent literature. *Water Research* 142, 26-45.  
512 Basha, S., Keane, D., Morrissey, A., Nolan, K., Oelgemoller, M., Tobin, J. (2010). Studies  
513 on the adsorption and kinetics of photodegradation of pharmaceutical compound,  
514 indomethacin using novel photocatalytic adsorbents (IPCA). *Industrial &*  
515 *Engineering Chemistry Research* 49, 11302-11309.  
516 Belhouchet, N., Hamdi, B., Chenchouni, H., Bessekhoud, Y. (2019). Photocatalytic  
517 degradation of tetracycline antibiotic using new calcite/titania nanocomposites.  
518 *Journal of Photochemistry & Photobiology A: Chemistry* 372, 196-205.

519 Briche, S., Derqaoui, M., Belaiche, M., El Mouchtari, E.M., Wong-Wah-Chung, P.,  
520 Rafqah, S. (2020). Nanocomposite material from TiO<sub>2</sub> and activated carbon for the  
521 removal of pharmaceutical product sulfamethazine by combined  
522 adsorption/photocatalysis in aqueous media. *Environmental Science and Pollution*  
523 *Research* 27, 25523–25534.

524 Calisto, V., Ferreira, C.I.A., Santos, S.M., Gil, M.V., Otero, M., Esteves, V.I. (2014).  
525 Production of adsorbents by pyrolysis of paper mill sludge and application on the  
526 removal of citalopram from water. *Bioresource Technology* 166, 335-344.

527 Chen, X.-L., Li, F., Chen, H., Wang, H., Li, G. (2020). Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> functionalized biochar  
528 as a heterogeneous catalyst for dyes degradation in water under Fenton processes.  
529 *Journal of Environmental Chemical Engineering* 8, 103905.

530 Dhiman, P., Dhiman, N., Kumar, A., Sharma, G., Naushad, M., Ghfar, A.A. (2019). Solar  
531 active nano-Zn<sub>1-x</sub>Mg<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> as a magnetically separable sustainable  
532 photocatalyst for degradation of sulfadiazine antibiotic. *Journal of Molecular*  
533 *Liquids* 294, 111574.

534 Do, T.C.M.V., Nguyen D.Q., Nguyen, K.T., Le, P.H. (2019). TiO<sub>2</sub> and Au-TiO<sub>2</sub>  
535 nanomaterials for rapid photocatalytic degradation of antibiotic residues in  
536 aquaculture wastewater. *Materials* 12, 2434.

537 Ferreira, C.I.A., Calisto, V., Otero, M., Nadais, H., Esteves, V.I. (2017). Removal of  
538 tricaine methanesulfonate from aquaculture wastewater by adsorption onto pyrolysed  
539 paper mill sludge. *Chemosphere* 168, 139-146.

540 Gaeta, M., Sanfilippo, G., Fraix, A., Sortino, G., Barcellona, M., Conti, G.O., Fragalà,  
541 M.E., Ferrante, M., Purrello, R., D'Urso, A. (2020). Photodegradation of Antibiotics  
542 by Noncovalent Porphyrin-Functionalized TiO<sub>2</sub> in Water for the Bacterial Antibiotic  
543 Resistance Risk Management. *International Journal of Molecular Science* 21, 3775.

544 Giang, C.N.D., Sebesvari, Z., Renaud, F., Rosendahl, I., Minh, Q.H., Amelung, W.  
545 (2015). Occurrence and Dissipation of the Antibiotics Sulfamethoxazole,  
546 Sulfadiazine, Trimethoprim, and Enrofloxacin in the Mekong Delta, Vietnam. *PLOS*  
547 *One* 10, 1-24.

548 Giraldo, A.L., Peñuela, G.A., Torres-Palma, R.A., Pino, N.J., Palominos, R.A., Mansilla,  
549 H.D. (2010). Degradation of the antibiotic oxolinic acid by photocatalysis with TiO<sub>2</sub>  
550 in suspension. *Water Research* 44, 5158-5167.

551 Gonçalves, A.A., Gagnon, G.A. (2011). Ozone Application in Recirculating Aquaculture  
552 System: An Overview. *Ozone-Science & Engineering* 33(5), 345-367.

553 Kosmulski, M. (2016). Isoelectric points and points of zero charge of metal (hydr)oxides:  
554 50 years after Parks' review. *Advances in Colloid and Interface Science* 238, 1-61.

555 Khraisheh, M., Kim, J., Campos, L., Al-Muhtaseb, A.H., Walker, G.M., Alghouti, M.  
556 (2013). Removal of carbamazepine from water by a novel TiO<sub>2</sub>-coconut shell  
557 powder/UV process: composite preparation and photocatalytic activity.  
558 *Environmental Engineering Science* 30, 515-526.

559 Kwon, G., Bhatnagar, A., Wang, H., Kwon, E.E., Song, H. (2020). A review of recent  
560 advancements in utilization of biomass and industrial wastes into engineered biochar.  
561 *Journal of Hazardous Materials* 400, 123242.

562 Lai, H.-T., Lin, J.-J. (2009). Degradation of oxolinic acid and flumequine in aquaculture  
563 pond waters and sediments. *Chemosphere* 75, 462-468.

564 Lazarotto, J.S., Brombilla, V.L., Silvestri, S., Foletto, E.L. (2020). Conversion of spent  
565 coffee grounds to biochar as promising TiO<sub>2</sub> support for effective degradation of  
566 diclofenac in water. *Applied Organometallic Chemistry*.  
567 <https://doi.org/10.1002/aoc.6001>.

568 Liu, S.-H., Tang, W.-T. (2020). Photodecomposition of ibuprofen over g-  
569  $C_3N_4/Bi_2WO_6/rGO$  heterostructured composites under visible/solar light. Science  
570 of the Total Environment 731, 139172.

571 Louros, V.L., Silva, C.P., Nadais, H., Otero, M., Esteves, V.I., Lima, D.L.D. (2020a).  
572 Oxolinic acid in aquaculture waters: Can natural attenuation through  
573 photodegradation decrease its concentration?. Science of the Total Environment  
574 749, 141661.

575 Louros, V.L., Silva, C.P., Nadais, H., Otero, M., Esteves, V.I., Lima, D.L.D. (2020b).  
576 Photodegradation of sulfadiazine in different aquatic environments – Evaluation of  
577 influencing factors. Environmental Research 188, 109730.

578 Mian, M., Liu, G. (2018). Recent progress in biochar-supported photocatalysts: synthesis,  
579 role of biochar, and applications. RSC Advances 8, 14237-14248.

580 Murgolo, S., Petronella, F., Ciannarella, R., Comparelli, R., Agostiano, A., Curri, M.L.,  
581 Mascolo, G. (2015). UV and solar-based photocatalytic degradation of organic  
582 pollutants by nano-sized  $TiO_2$  grown on carbon nanotubes. Catalysis Today 240,  
583 114-124.

584 Naciri, Y., Bouddouch, A., Bakiz, B., Taoufyq, A., Ezahri, M., Benhachemi, A. (2020).  
585 Photocatalytic degradation of sulfadiazine by  $Zn_3(PO_4)_2/BiPO_4$  composites upon  
586 UV light irradiation. Materials Today: Proceedings 22, 48-51

587 Nawaz, M., Miran, W., Jang, J., Lee, D.S. (2017). One-step hydrothermal synthesis of  
588 porous 3D reduced graphene oxide/ $TiO_2$  aerogel for carbamazepine  
589 photodegradation in aqueous solution. Applied Catalysis B: Environmental 203, 85-  
590 95.



591 Palominos, R.A, Mora, A., Mondaca, M.A., Pérez-Moya, M., Mansilla, H.D. (2008).  
592 Oxolinic acid photo-oxidation using immobilized TiO<sub>2</sub>. Journal of Hazardous  
593 Materials 158, 460-464.

594 Peñas-Garzón, M., Gómez-Avilés, A., Bedia, J., Rodriguez, J.J., Belver, C. (2019). Effect  
595 of Activating Agent on the Properties of TiO<sub>2</sub>/Activated Carbon Heterostructures for  
596 Solar Photocatalytic Degradation of Acetaminophen. Materials 12, 378-394.

597 Pereira, D., Rocha, L.S., Gil, M.V., Otero, M., Silva, N.J.O., Esteves, V.I., Calisto, V.  
598 (2021). In situ functionalization of a cellulosic-based activated carbon with magnetic  
599 iron oxides for the removal of carbamazepine from wastewater. Environmental  
600 Science and Pollution Research 28, 18314-18327.

601 Rigos, G., Nengas, I., Alexis, M., Troisi, G.M. (2004). Potential drug (oxytetracycline  
602 and oxolinic acid) pollution from Mediterranean sparid fish farms. Aquatic  
603 Toxicology 69, 281-288.

604 Rocha, L.S., Pereira, D., Sousa, É., Otero, M., Esteves, V.I., Calisto, V. (2020). Recent  
605 advances on the development and application of magnetic activated carbon and char  
606 for the removal of pharmaceutical compounds from waters: A review. Science of  
607 the Total Environment 718, 137272.

608 UNEP (2017). Frontiers 2017 Emerging Issues of Environmental Concern. United  
609 Nations Environment Programme, Nairobi:  
610 [https://www.unep.org/resources/frontiers-2017-emerging-issues-environmental-](https://www.unep.org/resources/frontiers-2017-emerging-issues-environmental-concern)  
611 [concern](https://www.unep.org/resources/frontiers-2017-emerging-issues-environmental-concern) (accessed on December 2020).

612 WHO (2020). World Health Organization about antimicrobial resistance:  
613 <https://www.who.int/news-room/fact-sheets/detail/antibiotic-resistance> (accessed  
614 on October 2020).

615 Xie, X., Li, S.; Zhang, H., Wang, Z., Huang, H. (2019). Promoting charge separation of  
616 biochar-based Zn-TiO<sub>2</sub>/pBC in the presence of ZnO for efficient sulfamethoxazole  
617 photodegradation under visible light irradiation. *Science of the Total Environment*  
618 659, 529–539.

619 Zhang, H., Wang, Z., Li, R., Guo, J., Li, Y., Zhu, J., Xie, X. (2017). TiO<sub>2</sub> supported on  
620 reed straw biochar as an adsorptive and photocatalytic composite for the efficient  
621 degradation of sulfamethoxazole in aqueous matrices. *Chemosphere* 185, 351-360.

622