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1 Modeling and optimization of a photocatalytic process: Degradation of 2 endocrine disruptor compounds by Ag/ZnO

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16
17 Keywords: artificial neural networks, optimization, photocatalysis, bisphenol-A.

18 19 **Abstract**

20 Artificial neural network (ANN) modeling was applied to study the photocatalytic degradation of
21 bisphenol-A. The operating conditions of the Ag/ZnO photocatalyst synthesis and its
22 performance were simultaneously modeled and subsequently optimized to target the highest
23 efficiency in terms of the degradation reaction rate. Two ANN models were developed to
24 simulate the stages of the photocatalyst synthesis and photodegradation performance,

25 respectively. A direct dependence between the two networks was also established, thus making
26 it possible to directly relate the degradation rate of the contaminant, not only to the
27 photodegradation conditions, but also to the photocatalyst synthesis conditions. In this respect,
28 an optimization study was carried out, by means of an evolutionary algorithm, in order to
29 identify the optimal synthesis and photodegradation conditions that would result in the
30 degradation of a maximal amount of the contaminant. Through this integrated approach it was
31 demonstrated that neural network models can be proven valuable tools in the evaluation,
32 simulation and, ultimately, the optimization of different stages of complex photocatalytic
33 processes towards the maximization of the efficiency of the synthesized photocatalyst.

34

35 **1 Introduction**

36 Endocrine-disrupting compounds (EDCs) is a class of chemical substances that pollute water
37 and other environmental resources. They are responsible for adverse developmental,
38 reproductive, neurological and immune side-effects on both humans and wildlife as they
39 interfere with the organism's endocrine system. Bisphenol-A (BPA) is an EDC that was used
40 initially (i.e., in the 1930's) as an estrogenic drug for birth control and later as a monomer in the
41 synthesis of polycarbonate as well as an additive in the synthesis of polyvinylchloride,
42 polyesters, epoxy resins, lacquer coatings, etc. It is these latter applications that have facilitated
43 the extensive, worldwide spread of this contaminant, presently detected in various aqueous
44 media including fresh and marine surface waters and groundwater (Flint et al., 2012; Klečka et
45 al., 2009).

46 Among the several studies on the removal of EDCs and pharmaceuticals from drinking water,
47 sunlight-induced photocatalytic degradation is an attractive approach that has gained
48 significant attention over the last years (Bohdziewicz et al., 2016; Esplugas et al., 2007;
49 Fernández et al., 2014; Sin et al., 2012; Sornalingam et al., 2016; Tijani et al., 2013). Yet, despite
50 the undisputed advantages of the process, such as its clean – non-chemical nature and its
51 relatively low cost, heterogeneous photocatalysis is a complex process whose efficiency is
52 related to a number of factors associated with the catalyst properties (e.g., crystal structure,
53 morphology, surface area, defect sites, polarity, active surface sites and reactive charges life-
54 time) and the photocatalytic reaction conditions (e.g., pH, contaminant concentration, catalyst
55 dose, light intensity). Hence, the control of the photocatalytic performance of UV/Metal Oxide
56 systems is not a trivial problem since it requires an optimal combination of the above

57 mentioned material and process characteristics and conditions. In this respect, the
58 development of an accurate robust mathematical model of the process becomes of profound
59 importance to the study and implementation of this decontamination technique.

60 Traditional modeling approaches of such systems are based on kinetic models that simulate the
61 contaminant degradation curves on the basis of a commonly adopted first-order kinetics
62 equation (Amani-Ghadim & Seyed Dorraji, 2015; Rosenfeldt & Linden, 2004; R. Wang et al.,
63 2009). On the other hand, alternative modeling methodologies (e.g., empirical models or
64 response surface methodologies) (Asl et al., 2012; Babaei et al., 2011; Kiattisaksiri et al., 2015;
65 Lee & Hamid, 2015; Merabet et al., 2016) are constantly gaining ground in the area, mainly due
66 to the complex nature of the photodegradation processes and the lack of thorough
67 understanding of all the mechanisms involved, which inhibits the development of generalized
68 powerful mechanistic models. Among these alternatives, Artificial Neural Network models
69 display an evergrowing presence in the most recent relevant studies.

70 Artificial Neural Networks (ANN) are powerful tools that can be implemented on a set of raw
71 experimental data to establish non-linear mathematical relations between the input/output of
72 the process. They belong to the general class of 'data-driven models' (DDM), which attempt to
73 create connections between the input variables and the responses of a system, without
74 requiring any prior knowledge on the underlying physical phenomena (Solomatine et al., 2008).

75 Other advantages of this class of models are their ability to extract and recognize patterns in
76 data, as well as their rather quick and simple development and implementation to completely
77 different processes.

78 Under the condition of existence of a sufficient number of experimental data, ANN models can
79 be proven quite efficient and accurate, both in correlating the existing data as well as in
80 predicting the system behavior (within the limits of the explored experimental space), while
81 they can also be easily customized to different systems. They are commonly developed with the
82 aid of specifically designed software or software package toolboxes (e.g., the ANN toolbox of
83 Matlab®), which are simple to use and quite flexible in terms of the customization of the model
84 structure and characteristics (Sivanandam et al., 2006).

85 A review of the implementation of ANN on heterogeneous photocatalytic water and
86 wastewater treatment processes was published by Khataee and Kasiri (2010). The accuracy of
87 ANN models was also assessed in a recent study by Amani-Ghadim and Seyed Dorraji (2015),
88 who compared three different model types, namely a kinetic model, an empirical model and an
89 ANN model on the photodegradation of Acid blue 9 using UV/ZnO. In this study, the authors
90 investigated the effect of different factors (i.e., contaminant initial concentration, ZnO content,
91 light intensity, pH and time) on the photodegradation efficiency and concluded that ANN
92 modeling allows an accurate description of the photocatalytic process without the necessity to
93 resort to complex mathematical descriptions of the kinetics.

94 Traditionally, ANN models have been applied to photocatalytic degradation processes in order
95 to study the effect of a variety of reaction conditions on the photocatalytic performance by
96 means of percentage of degradation or removal efficiency. It is only recently that the apparent
97 reaction rate constant of a first-order photocatalytic degradation curve was considered as the
98 simulated response of the developed ANN model (Behnajady & Eskandarloo, 2015; Delnavaz,
99 2015). The characteristics of a series of similar recent studies are summarized in Table 1.

100 As can be seen, ANN models can be used to assess the effect of numerous important factors of
101 the process, such as light intensity, organic/inorganic ions concentration and oxygen dose,
102 which influence the photocatalytic performance but are rarely considered in kinetic models. For
103 instance, Vaez et al. (2015) studied the effect of anions naturally present in wastewater (i.e.,
104 sulfate SO_4^{2-} , chloride Cl^- , bicarbonate HCO_3^- and carbonate CO_3^{2-}) and peroxide, on the
105 photodegradation of Acid Red 73 on UV/ TiO_2 nanoparticles immobilized on sackcloth fiber. In
106 another noteworthy example, Tanasa et al. (2013) successfully studied the effect of both
107 photocatalyst properties (i.e., crystallite size, surface area and absorption edge) and reaction
108 conditions (i.e., dye initial concentration, time and catalyst dose) on the color removal of Eosin
109 Y in UV/ ZnO/SnO_2 systems.

110 In the present work, a novel modeling framework is proposed for the study of a photocatalytic
111 degradation process of a water contaminant. In this respect, the two major stages of the
112 photocatalytic process, namely the photocatalyst synthesis and the contaminant degradation
113 experiments, are decoupled in order to separately assess the effects of the factors affecting
114 these two process stages on the overall photocatalytic efficiency of the synthesized
115 photocatalyst. Two artificial neural networks are developed for the modeling of these two
116 stages, linked together by the fact that the output of the ANN model on the photocatalyst
117 synthesis is, at the same time, an input for the ANN model on the photodegradation
118 experiments. In a subsequent optimization analysis, the two models are separately optimized in
119 the inverse order (i.e., starting from the model on the photodegradation tests), thus connecting
120 the photodegradation efficiency (i.e., related to the objective function of the first optimization

121 study on the second ANN model) with the photocatalyst synthesis conditions (i.e., optimal
122 decision variables of the second optimization study on the first ANN model).

123 The system under study concerns the use of silver-modified ZnO particles (Ag/ZnO) as effective
124 catalysts for the photodegradation of BPA in water. ZnO, charged with silver nanoparticles
125 (AgNPs), is a prominent photocatalyst that has been employed in several contaminant
126 photodegradation studies due to its decreased charge-carriers recombination rate, increased
127 photostability and efficiency (Georgekutty et al., 2008; J. Wang et al., 2011; Xie et al., 2010).

128 The detailed characteristics of the experimental system have been extensively presented in a
129 recent publication (Jasso-Salcedo et al., 2016) and will not be the subject of the present work.

130 To the best of the authors' knowledge, this is the first time that a two-stage, de-coupled ANN
131 modelling framework is proposed for the study and, subsequently, the optimization of the
132 photocatalytic degradation of an endocrine disrupting contaminant. The proposed approach
133 allows for the evaluation of the effects of the factors of the two principal stages of the
134 photodegradation process (i.e., the catalyst synthesis and the degradation experiments) on the
135 final photodegradation efficiency, by distinguishing these two stages without completely
136 isolating them from the overall process.

137

139 **Table 1.** Neural Network modeling studies of the photocatalytic performance on the degradation of water contaminants.

Photocatalyst	Model contaminant	ANN Topology (In:Hid:Out)	Data number	Input / Factors	Output / Response	Reference
ZnO	Acid Blue 9	5:9:1	152	AB9, pH, ZnO, UV intensity	Degradation efficiency (%)	Amani-Ghadim and Seyed Dorraji (2015)
ZnO/Montmorillonite K10	Disperse Red 54 (DR54)	5:10:1	N/A	DR54, ZnO/MMT, time	Decolorization efficiency (%)	Kiransan et al. (2015)
ZnO/Montmorillonite K10	Basic yellow 28 (BY28)	3:14:1	N/A	BY28, ZnO/MMT dosage, UV radiation time	Decolorization efficiency (%)	Kiransan et al. (2015)
TiO ₂	Acid Red 27	4:8:1	56	TiO ₂ , AR27, pH, UV intensity	Reaction rate constant (Kap)	Behnajady and Eskandarloo (2015)
TiO ₂ -Light expanded clay aggregates	Phenol	5:6:4:2	325	Reaction time, Phenol, pH, TiO ₂ , UV intensity	Photocatalytic reactor efficiency (%) and Kinetic constant (Kapp)	Delnavaz (2015)
TiO ₂ /sackcloth fibre	Acid Red 73	5: 15:1	300	pH, time, anion, H ₂ O ₂ , AR73 concentration	Photocatalytic efficiency (%)	Vaez et al. (2015)
SnO ₂ /Fe ₃ O ₄	Phenol red	4:20:30:20:1	30	SnO ₂ /Fe ₃ O ₄ , phenol red, stirring intensity, UV intensity	Dye removal (%)	Sargolzaei et al 2015
TiO ₂ /ZrO ₂	Carbamazepine (CBZ)	4:5:1	130	TiO ₂ /ZrO ₂ , pH, reaction time, CBZ	CBZ removal (%)	Das et al. (2014)
TiO ₂	Chromium (Cr (VI))	4:4:1	558	Cr(VI), pH, TiO ₂ , irradiation time	Photocatalytic reduction Cr (VI) (%)	Sabonian and Behnajady (2014)
TiO ₂	N,N-diethyl-m-toluamide (DEET)	3:13:1	17	TiO ₂ , DEET, UV intensity	Photocatalytic oxidation (%)	Antonopoulou and Konstantinou (2013)
TiO ₂	Total phenolic compounds (TPh)	3:12:1	17	TiO ₂ , TPh, UV intensity	Photocatalytic oxidation of TPh (%)	Antonopoulou et al. (2012)
TiO ₂	17 α -ethynylestradiol (EE2)	5:13:1	222	Reaction time, TiO ₂ , EE2, water dissolved organic carbon, water conductivity	EE2 conversion (%)	Frontistis et al. (2012)
TiO ₂	4-nitrophenol (4-NP)	4:14:1	147	Nano TiO ₂ , time, UV intensity, 4-NP	Removal (%)	Ghanbary et al. (2012)
TiO ₂	Reactive black 5 (RB5)	4:10:1	N/A	pH, TiO ₂ dose, RB5, time	Photocatalytic efficiency (%)	Dutta et al. (2010)

141 **2 Methodology**

142 **2.1 Data collection**

143 **2.1.1 Preparation of Ag/ZnO**

144 The Ag/ZnO photocatalyst was prepared by photodeposition (PD) and impregnation (IMP)
145 methods (Jasso-Salcedo et al., 2014). For both methods, a suspension containing ZnO and
146 stabilized silver nanoparticles (AgNPs) was adjusted at desired initial pH values using 0.1N HCl
147 and/or 0.5 N NaOH. The suspension was stirred under UV irradiation or in darkness, for PD and
148 IMP methods, respectively. Then the sample was submitted to centrifugation/re-dispersion
149 cycles in distilled water and ethanol solutions several times to remove the free AgNPs (i.e., not
150 attached to the ZnO surface). The actual weight percentage of AgNPs that were finally attached
151 to the ZnO surface was calculated by the following expression:

$$152 \quad W_{\text{Ag}} \% = \frac{W_{\text{Ag}}}{W_{\text{Ag}} + W_{\text{Zn}}} 100 \quad (1)$$

153 where the quantities of Ag and Zn were obtained from elemental quantification using
154 inductively coupled plasma spectrometry (ICP-OES, 730-ES, Varian Inc.) at 328 nm and 213.9
155 nm, respectively. Before the analysis, the samples were submitted to acid digestion (69% Nitric
156 acid), diluted with DI H₂O and filtered (0.45 μm).

157 **2.1.2 Photocatalysis experiments**

158 An aqueous solution of BPA and photocatalyst was mechanically stirred for 10 min in darkness
159 and then irradiated at different wavelengths, namely at 254, 302 or 365 nm using a UV lamp
160 (3UV-38, UVP Inc.) and at 450 nm using a fluorescent lamp (F8T5/CW, Hampton Bay). The

161 experiments were carried out in a dark box, with the lamp placed at a distance of 8 cm above
162 the sample, at room temperature and without external oxygen supply (Jasso-Salcedo et al.,
163 2014). Samples were then collected at regular time intervals and centrifuged at 3,000 rpm for
164 10 min to recover the photocatalyst powder. The liquid samples were filtered (0.45 μm) before
165 liquid chromatography (HPLC 1200 Series, Agilent Technologies) analysis.

166 The apparent kinetic rate constant of the BPA degradation was obtained as follows: the
167 experimental data (i.e, BPA concentration vs time plots) were initially approximated by an
168 exponential decay function, as shown in Eq.(2):

$$169 \quad C_N = a \exp(bt); \quad b < 0 \quad (2)$$

170 where C_N denotes the normalized BPA concentration (C/C_0). A least squares regression provided
171 the values of α and b for each experiment. In order to associate the BPA degradation curves
172 with a rate constant, the differential form of Eq.(2) was then transformed into a typical rate
173 function of order n :

$$174 \quad r \left(= -\frac{dC_N}{dt} \right) = k_{app} C_N^n \quad (3)$$

175 In the above equation, k_{app} and n are the apparent kinetic rate constant and the order of the
176 reaction, respectively and r denotes the rate of the reaction. The values of k_{app} and n can be
177 estimated by substituting Eq.(2) into Eq.(3):

$$178 \quad \begin{cases} n = 1 \\ k_{app} = -b \end{cases}$$

179 The first order rate of the BPA degradation was also confirmed by plotting $\ln(r)$ vs $\ln(C_N)$ and
180 estimating the regression parameters of the produced straight line, according to the linearized
181 form of Eq.(3):

182 $\ln(r) = \ln(k_{app}) + n \ln(C_N)$ (4)

183 Note that the value of the correlation coefficient, R , of this linear regression is given, for each
184 experiment, in Table 5, along with the values of the experimental measurements.

185 **2.2 Artificial neural network modeling**

186 A neural network is a cluster of processing nodes (i.e., neurons) arranged in several layers and
187 interconnected in a variety of topologies, following the paradigm of the functionality of the
188 human brain. The successful development and implementation of an ANN model relies onto
189 three principal conditions, each one with its own significance for the accuracy and efficiency of
190 the developed model:

- 191 I. Correct identification of the input and output variables of the system, also called factors
192 and responses, respectively. The selection of the principal factors (i.e., the ones with the
193 greatest effect on the targeted response) from all possible candidates is a procedure
194 that requires a minimum knowledge of the actual process. Its importance lies in the fact
195 that the number and nature of the selected factors will affect, on the one hand, the
196 number of required experimental data (i.e., the more factors considered, the greater
197 the number of data required for an accurate model development), and on the other
198 hand, will define whether important effects on the measured response have been
199 omitted. In the case where prior knowledge on the process is completely absent, a small
200 number of exploratory experiments can be carried out.
- 201 II. Definition of the experimental space and execution of a set of experiments for the
202 acquisition of data. Given that the main factors of the process have been correctly

203 identified and under the assumption that there exists a correlation between these
204 factors and the targeted response of the system, an ANN model can identify this
205 correlation on the basis of a set of experimental data. Evidently, the ability of the ANN
206 to successfully correlate the input(s) (i.e., factors) and output(s) (i.e., response(s)) is
207 directly proportional to the number of available data. On the other hand, the number of
208 experiments that can be carried out is always subject to feasibility constraints (e.g., time
209 and/or cost limitations, etc.) that may dictate the studied process. Hence, the
210 implementation of an experimental design strategy can become invaluable during this
211 second stage of the model development procedure. The Design of Experiments (DoE)
212 approach enables to obtain a maximum amount of information from a given predefined
213 experimental effort. Typical DoE strategies include full- or fractional-factorial designs,
214 central composite designs, Box–Behnken designs , Plackett– Burman (PB) designs, D-
215 optimal and E-optimal designs, etc. (Ferreira et al., 2007; Georgakis, 2013; Heiligers,
216 1994; Witek-Krowiak et al., 2014).

217 III. Identification of the topology of the ANN: The structure of the network, in terms of the
218 number and size of the hidden layers, as well as its characteristics (i.e., training
219 algorithm, type of transfer functions, etc.), display a significant effect on the accuracy of
220 the model. To identify these parameters, most studies follow a trial and error procedure
221 where different topologies of the ANN are tested until satisfactory accuracy has been
222 achieved. Note that the random initialization of the values of the network parameters
223 (e.g., the neuron’s weights) as well as of the data separation (c.f. next paragraph) must
224 be taken into account during this procedure.

225 Once the experimental data have been acquired and the factors/responses and architecture of
226 the ANN model have been defined, the development of the model proceeds via a series of
227 subsequent training (i.e., parametric identification) steps. In general, the accuracy of such
228 models is assessed in terms of different statistical magnitudes, such as the Mean Square Error,
229 MSE, or the correlation coefficient, R , calculated on the basis of the comparison of the model
230 responses and the respective experimental targets. These latter are divided into three distinct
231 subsets that serve for the training, validation and testing of the network, respectively. The
232 training data set is used for the identification of the model parameters while the test data set is
233 used to assess the accuracy of the model on a set of data different than the ones used for the
234 training and validation processes. The validation data set is used to avoid overfitting
235 phenomena by monitoring the error (i.e., on this data set) throughout the training process. This
236 error normally decreases along with the training set error. An increase on the validation error
237 for a number of sequential epochs (i.e., training *passes* of the network) is an indication of
238 overfitting that triggers the stopping of the training process, returning the network (i.e., the
239 values of weights and biases) corresponding to the minimum value of the validation error. In
240 the present work, the number of sequential epochs of increasing validation error before
241 stopping the training of the network was set to seven.

242 Among the various types of existing ANNs, the most commonly encountered in physicochemical
243 process modeling is the feed-forward (i.e., the responses of each layer are used as inputs of the
244 next layer) back-propagation (i.e., the measured error at the output layer is back transferred to
245 re-adjust the model parameter values) network, while the sigmoidal (e.g., logarithmic sigmoidal
246 or tangent hyperbolic sigmoidal) and linear transfer functions are widely applied on the hidden

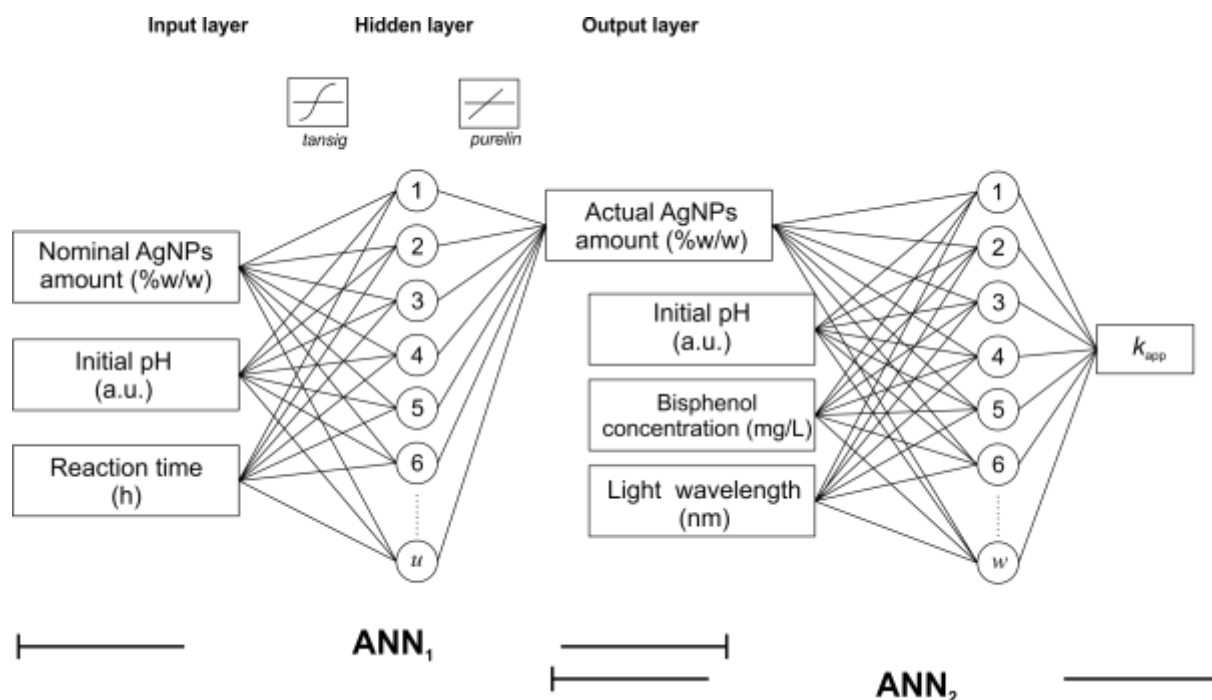
247 and output layers, respectively (Cheng & Titterington, 1994; Haykin, 1994; Meireles et al., 2003;
248 Sivanandam et al., 2006). Additional details on the principles and the characteristics of neural
249 networks can be found in the relevant literature (Cheng & Titterington, 1994; Haykin, 1994;
250 Meireles et al., 2003; Sivanandam et al., 2006).

251 Photocatalytic processes are greatly influenced by both catalyst properties and reaction
252 conditions. These effects are traditionally studied separately (see Table 1), probably due to the
253 complexity of assessing them simultaneously in a single study. An exception to this rule is the
254 work of Tanasa et al. (2013), who studied the system of Eosin Y dye photocatalytic degradation
255 using ZnO/SnO₂, taking into account the effects of crystallite size, surface area, absorption
256 edge, catalyst dose and total organic carbon values in their model that was developed on the
257 basis of a set of 547 experimental data. In addition, another commonly adopted practice is the
258 consideration of the irradiation time as a factor in the modeling of the percentage of
259 contaminant degradation (i.e., response). Given that the percentage of contaminant
260 degradation will normally increase with the reaction time, this approach finally leads to a rather
261 obvious correlation that, in turn, may come in the cost of missing other important effects of
262 different factors.

263 In the present work, a model development is presented that does not comply with the above
264 commonly adopted approaches. In order to combine the effects of both important stages of the
265 photocatalytic process, namely the catalyst synthesis and the photodegradation experiments, a
266 two-stage decoupled ANN model is developed where the response of the first network
267 becomes a factor for the second network. Thus, in the first stage of the model, the effects of
268 three operating conditions of the synthesis of Ag/ZnO (i.e., nominal silver concentration, pH

269 and reaction time, which were identified in Jasso-Salcedo et al., 2014 as the most significant
270 parameters of the process) on the actual amount of Ag attached on the surface of ZnO of the
271 synthesized photocatalyst were assessed in terms of an initial neural network, henceforth
272 called ANN₁. In the second stage of this modelling framework, the effect of the actual amount
273 of Ag attached on the surface of ZnO, pH of the medium, initial contaminant concentration and
274 wavelength of light on the photodegradation performance of the photocatalyst were assessed
275 in terms of a second neural network, ANN₂. A direct dependence between the two networks
276 was established by directly introducing the response of ANN₁ as a factor of ANN₂. The
277 photodegradation performance (i.e., the response of ANN₂) was evaluated in terms of an
278 apparent kinetic rate constant, k_{app} , of the degradation reaction of BPA. This way, the
279 photocatalyst synthesis conditions were directly associated to its final photodegradation
280 performance, taking simultaneously into account the effects of the photodegradation
281 conditions. Note that, since the evaluation of the performance of the photocatalyst was based
282 on the rate of degradation of the contaminant, there was no need to consider the irradiation
283 time among the factors of the photodegradation process, which was kept constant for all
284 experiments and equal to 120 min.

285 The experimental ranges of all factors of the two sub-models (i.e., ANN₁ and ANN₂) are given in
286 Tables 2 and 3, respectively. Note that for the modification experiments of ZnO, a central
287 composite design was employed. The photocatalyst concentration used for the degradation
288 tests was set to 1 g/L. A general schematic of the proposed modeling framework is shown in
289 Scheme 1.



290

291 Scheme 1. Description of the input/output characteristics and connecting points of the two

292 ANN models.

293

294 **Table 2.** Experimental range of the Ag/ZnO photocatalyst synthesis conditions

Input variables	Photodeposition	Impregnation
Nominal amount AgNPs (% w/w)	0.1-1	0.1-5
Initial pH	7-11	7-11
Time (h)	0.5-1	2-5

295

296 **Table 3.** Experimental range of the photodegradation test conditions

Input variables	
Initial pH	2.8 to 10.5
Actual amount AgNPs (%w/w)	0-1.2
Bisphenol-A (mg/L)	10-40
Wavelength (nm)	254, 302, 365 and 450

297

298 **2.2.1 Neural network structure**

299 A multi-layer feedforward network with Levenberg-Marquardt learning algorithm was used in
300 this study. The experimental data corresponding to each model were randomly divided into
301 training, validation and testing subsets (50 %, 25 % and 25 % of data, respectively). All data
302 were normalized in the range [-1:1] prior to their introduction into the models.

303 The topology of the network models, denoted as (In:Hid:Out), corresponds to the numbers of
304 neurons in the input, hidden and output layers, respectively. Several configurations of the
305 network were tested to determine the best number of neurons in the hidden layer(s), based on
306 the values of the MSE of the data sets. The MSE value between the ANN model predictions and
307 the experimental data is typically calculated by the expression:

$$308 \quad MSE = \frac{\sum_{j=1}^N (y_j^{\text{mod}} - y_j^{\text{exp}})^2}{N} \quad (5)$$

309 where the exponents 'mod' and 'exp' denote the outputs of the model (i.e., the responses) and
310 the experiment (i.e., the targets), respectively and N is the total number of experimental data.

311 Note that, in the present work, log-sigmoidal and linear transfer functions were used for hidden
312 and output layers, respectively. The Neural Network Toolbox of the commercial software
313 package MATLAB 8.3.0.532 (academic license) was used for the development of the models.

314 **2.3 Optimization study**

315 An ultimate purpose of process models, especially data-driven models, is their implementation
316 in an optimization study in order to identify the combination of the different process conditions
317 that will result to the desired properties/performance of the product/process under study.

318 Among the plethora of different mathematical methods and techniques that have been

319 developed for the treatment of optimization problems, evolutionary algorithms constitute a
320 powerful approach with specific advantages and disadvantages.

321 In general, an evolutionary algorithm (EA) is based on the principle of the continuous
322 improvement of a criterion (i.e., the optimization criterion) of the individuals of a population.

323 The initial population is composed of a large set of randomly selected individuals (e.g.

324 experimental conditions), which are characterized by a measured property or model response

325 (e.g., the degradation efficiency corresponding to each of these experiments). The population is

326 classified from the best individual to the worst, according to its corresponding value of the

327 criterion and depending on whether the problem is a minimization or a maximization one, and

328 is subsequently subjected to a series of cycles of improvement of this criterion. The best

329 individuals are combined to generate new ones that might perform better, while the worst

330 individuals are removed from the population after each cycle and the procedure continues until

331 the population has “evolved” to such a point where the desired convergence to an optimal has

332 been achieved. Detailed information on the theoretical basis of EAs for mono- and multi-

333 objective optimization, applied on physicochemical processes, can be found in the relevant

334 literature (Camargo et al., 2011; Fonteix et al., 1995; Viennet et al., 1996; Xi et al., 2013). EAs

335 have also been successfully implemented in the optimization study of the degradation of

336 phenol by a combined photocatalysis/electro-Fenton system (Khataee et al., 2014).

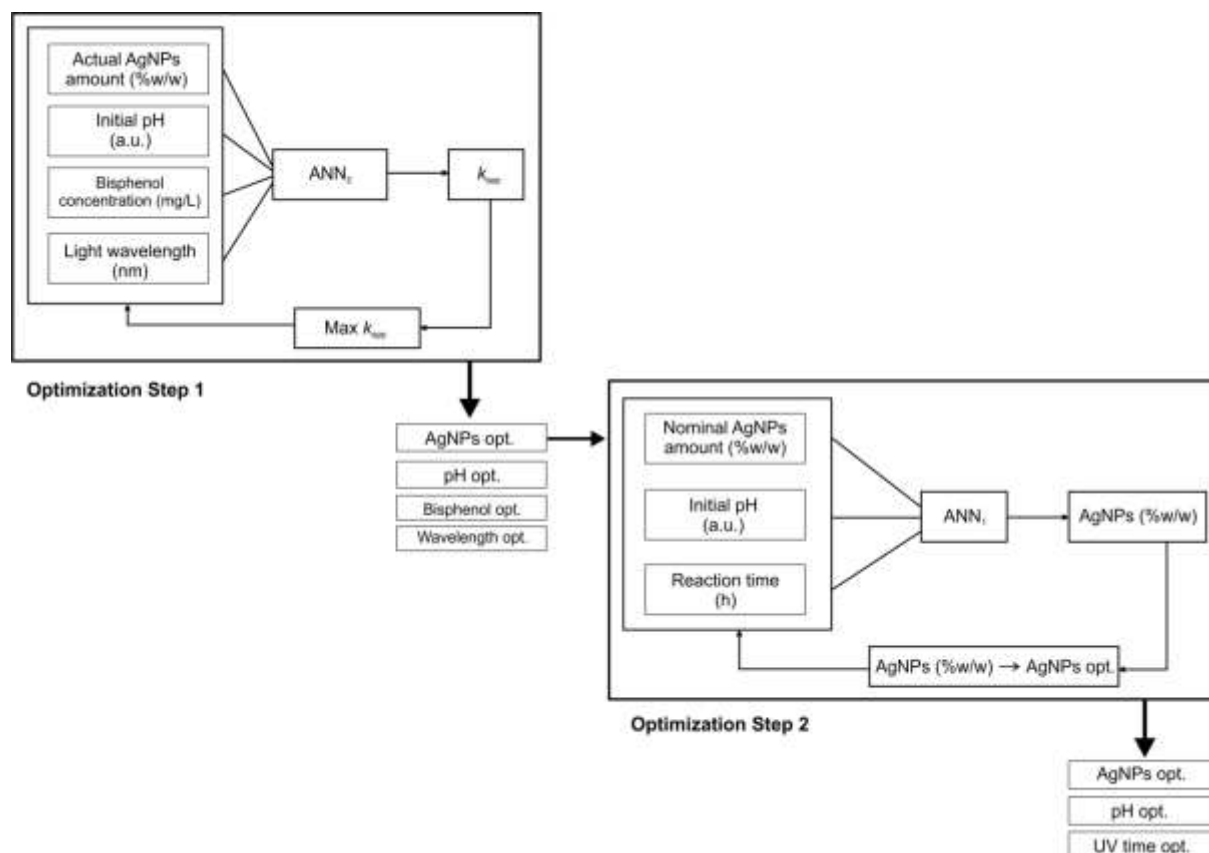
337 In the present work, an optimization study, on the basis of an EA, was also carried out in order

338 to identify the optimal catalyst synthesis and photodegradation conditions that would result to

339 the highest photodegradation rate of BPA. In accordance to the two-stage structure of the

340 model, the optimization was also carried out in two consecutive steps, following an *inverse*

341 *direction*. In this respect, an initial optimization problem was solved on the basis of ANN₂ in
342 order to identify the different photodegradation conditions that would result to a maximum
343 degradation rate of BPA. Among these conditions, the pH, BPA concentration and light
344 wavelength can be directly set to their optimized values, according to the results of this first
345 optimization study. On the other hand, the actual silver content of the photocatalyst depends
346 on the conditions of the photocatalyst synthesis process. Hence, a second optimization problem
347 was subsequently solved, via the implementation of an EA on the basis of ANN₁, in order to
348 identify the photocatalyst synthesis conditions that would result in the optimal amount of
349 attached AgNPs on the ZnO surface, as defined by the output of the first optimization run. Thus,
350 both important stages of the overall process (i.e., the synthesis of the photocatalyst and its
351 subsequent use in the photodegradation experiments) were taken into account and their
352 optimal conditions were identified in view of a maximal photodegradation rate of BPA. The
353 overall optimization approach is schematically depicted in Scheme 2.



354
 355 **Scheme 2.** Methodology used on the Evolutionary Algorithm - ANN coupled optimization approach on this study.
 356

357 **3 Results and discussion**

358 The development of the two ANN sub-models was based on a total of 63 experiments for ANN₁
 359 and 27 experiments for ANN₂, divided into the two methods of the photocatalyst synthesis (i.e.,
 360 PD and IMP methods) as shown in Tables 4 and 5. On the basis of these experimental data, the
 361 identification of the optimal network topologies initially took place and subsequently the ANN
 362 models were tested and validated before their implementation into the optimization study.
 363
 364

365 **Table 4.** Experimental conditions for the synthesis of Ag/ZnO photocatalyst and actual amount of Ag attached to the ZnO surface as measured
 366 experimentally and predicted theoretically by the ANN₁ models

Nominal Ag %w/w	pH	Reaction time (min)	Attached Ag %w/w (experimental)	Attached Ag %w/w (ANN ₁ model)	Nominal Ag %w/w	pH	Reaction time (min)	Attached Ag %w/w (experimental)	Attached Ag %w/w (ANN ₁ model)
Photodeposition method					Impregnation method				
0.3573	7	30	0.320	0.327	0.1072	7	60	0.100	0.116
0.3573	7	60	0.342	0.348	0.1072	7	120	0.106	0.121
0.1073	7	30	0.082	0.084	0.1072	7	300	0.094	0.094
0.1073	7	60	0.107	0.102	1.0623	7	60	1.179	1.179
1.0623	7	30	0.991	0.920	1.0623	7	120	1.203	1.203
1.0623	7	60	1.093	1.099	1.0623	7	300	0.820	0.807
0.3573	9	30	0.358	0.356	5.095	7	60	0.521	0.522
0.3573	9	60	0.375	0.378	5.095	7	120	0.585	0.773
0.1073	9	30	0.062	0.062	5.095	7	300	0.668	0.671
0.1073	9	60	0.074	0.075	0.1072	9	60	0.099	0.093
1.0623	9	30	1.170	1.104	0.1072	9	120	0.110	0.110
1.0623	9	60	1.132	1.130	0.1072	9	300	0.096	0.100
0.3573	11	30	0.454	0.451	1.0623	9	60	0.970	1.012
0.3573	11	60	0.426	0.397	1.0623	9	120	1.192	1.188
0.1073	11	30	0.091	0.092	1.0623	9	300	1.194	1.193
0.1073	11	60	0.116	0.121	5.095	9	60	0.423	1.044
1.0623	11	30	1.183	1.182	5.095	9	120	0.494	0.336
1.0623	11	60	1.147	1.137	5.095	9	300	0.571	0.580
0.3573	7	45	0.320	0.325	0.1072	11	60	0.116	0.105
0.1073	9	45	0.074	0.071	0.1072	11	120	0.121	0.121
1.0623	9	45	1.132	1.132	0.1072	11	300	0.116	0.120
0.3573	9	45	0.362	0.365	1.0623	11	60	0.239	0.239
0.1073	7	45	0.096	0.096	1.0623	11	120	0.366	0.561
0.1073	11	45	0.103	0.102	1.0623	11	300	1.108	1.101
1.0623	7	45	1.050	1.054	5.095	11	60	0.374	0.375

1.0623	11	45	1.162	1.161	5.095	11	120	0.389	1.144
0.3573	9	45	0.371	0.365	5.095	11	300	0.498	0.503
0.3573	9	45	0.368	0.365	1.0623	9	120	1.169	1.188
0.3573	9	45	0.385	0.365	1.0623	9	120	1.223	1.188
0.3573	9	45	0.357	0.365	1.0623	9	120	1.023	1.188
0.3573	9	45	0.362	0.365	1.0623	9	120	1.179	1.188
					1.0623	9	120	1.167	1.188

367

368

369 **3.1 Selection of optimal network topology**

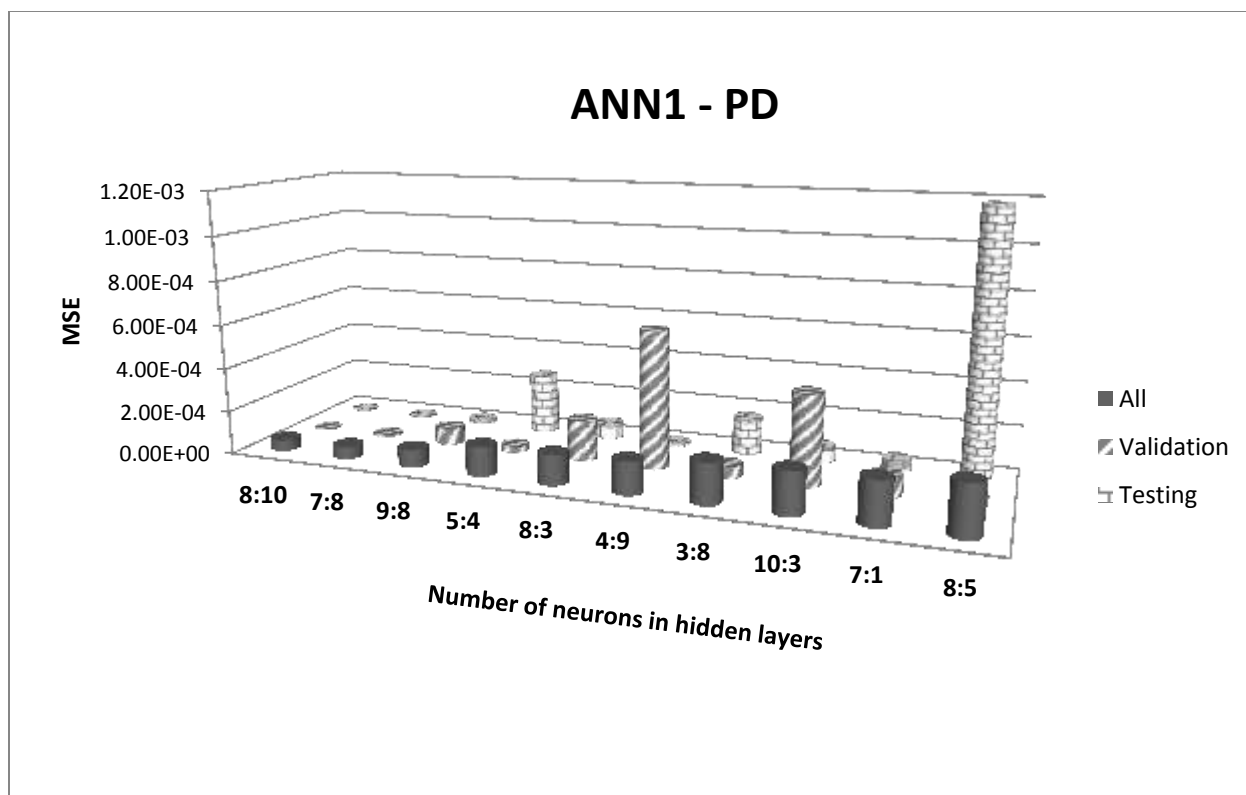
370 The selection of the network topology was based on a typical trial and error approach where the number of neurons of the hidden
371 layer(s) was varied in the range 1-20 (i.e., for a single hidden layer) and 1:1-10:10 (i.e., for two hidden layers) and the accuracy of the
372 developed model was assessed in terms of the MSE values between the model predictions and the experimental data. An example
373 of the results obtained by this procedure is shown in Figure 1 for the ANN₁ model and the PD method. In this Figure, the ten best
374 (i.e., corresponding to the lowest MSE values) network configurations are shown in a MSE-increasing order. Note that the errors
375 corresponding to all data, validation and testing data sets are shown in order to verify the consistency of the model performance vis-
376 à-vis the different data sets. Each network topology was run 50 times (i.e., 50 different ANNs with the same topology were
377 developed and evaluated) and the average value of MSE was used for comparison, in order to avoid random correlation effects.

378 **Table 5.** Experimental conditions of bisphenol-A degradation and apparent kinetic rate constant k_{app} used on the
 379 ANN₂ model

pH	Actual amount Ag (%w/w)	BPA (mg/L)	Wavelength (nm)	R ¹	Reaction order n	k_{app} experimental	k_{app} predicted (ANN ₂ models)	
							ANN ₂ -PD	ANN ₂ -IMP
²Pure ZnO photocatalyst								
10.5	0	10	302	0.973	0.887	4.53E-03	4.53E-03	5.74E-03
10.5	0	10	450	0.988	0.999	6.23E-04	2.27E-04	6.23E-04
7.5	0	10	254	0.992	1.161	2.55E-03	2.79E-03	2.55E-03
2.81	0	10	254	0.999	1.019	3.83E-03	3.78E-03	4.59E-03
4.27	0	10	254	0.999	0.999	3.89E-03	3.78E-03	3.89E-03
9.38	0	10	254	0.986	1.001	4.97E-03	4.92E-03	4.97E-03
10.5	0	10	254	0.999	1.022	7.55E-03	7.44E-03	7.87E-03
7.25	0	20	254	0.999	1.031	1.75E-03	1.73E-03	1.75E-03
8.53	0	20	302	0.990	1.013	1.10E-03	1.21E-03	1.67E-03
8.53	0	20	365	0.999	0.992	2.31E-03	2.41E-03	2.31E-03
Photodeposition method							ANN₂-PD	
10.5	1.093	10	254	0.999	1.018	1.02E-02	1.01E-02	
10.5	1.093	10	302	0.999	1.006	1.86E-02	1.52E-02	
10.5	1.093	10	365	0.990	1.002	1.54E-02	1.41E-02	
10.5	1.093	20	254	0.999	1.022	4.97E-03	5.33E-03	
7.51	1.093	40	254	0.982	0.970	1.73E-03	1.24E-03	
10.5	1.147	10	254	0.999	1.024	1.21E-02	1.11E-02	
10.5	1.147	10	302	0.999	1.011	1.85E-02	1.61E-02	
10.5	1.147	10	365	0.999	1.008	1.02E-02	1.01E-02	
10.5	1.147	10	450	0.999	1.046	1.86E-02	1.52E-02	
7.2	1.147	40	254	0.999	0.956	1.54E-02	1.41E-02	
Impregnation method							ANN₂-IMP	
10.5	1.203	10	254	0.999	1.007	8.28E-03	9.25E-03	
10.5	1.203	10	302	0.999	0.995	9.37E-03	9.37E-03	
10.5	1.203	10	365	0.999	0.993	1.10E-02	9.02E-03	
10.5	0.366	10	254	0.999	1.006	8.42E-03	8.36E-03	
10.5	0.366	10	302	0.999	0.992	1.22E-02	1.22E-02	
10.5	0.366	10	365	0.999	1.006	1.37E-02	1.17E-02	
10.5	0.366	10	450	0.999	1.009	1.28E-03	1.28E-03	

380 ¹ Correlation coefficient of the linear regression of the experimental data, as explained in section 2.1.

381 ² Common experiments, used for the development of both PD and IMP ANN₂ models.



382
 383 **Figure 1.** MSE for all data, validation and test datasets as function of neurons in the hidden layer on the network
 384 topology for the developed ANN1 model (photodeposition method).
 385

386 The numerical data corresponding to Figure 1, as well as the data corresponding to the other
 387 three models (i.e., ANN₁-IMP, ANN₂-PD and ANN₂-IMP) are given in Table S.1 of the
 388 supplementary material section. The network topologies that were retained according to this
 389 procedure are shown in Table 6:

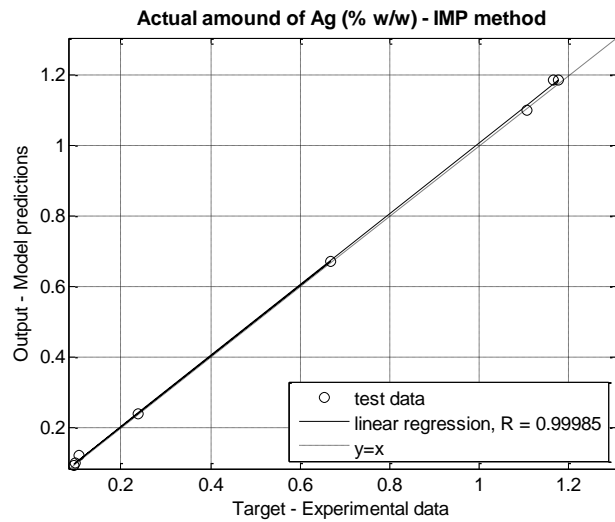
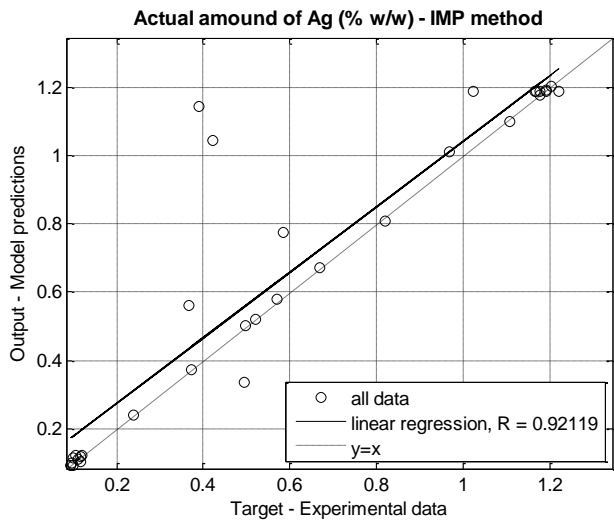
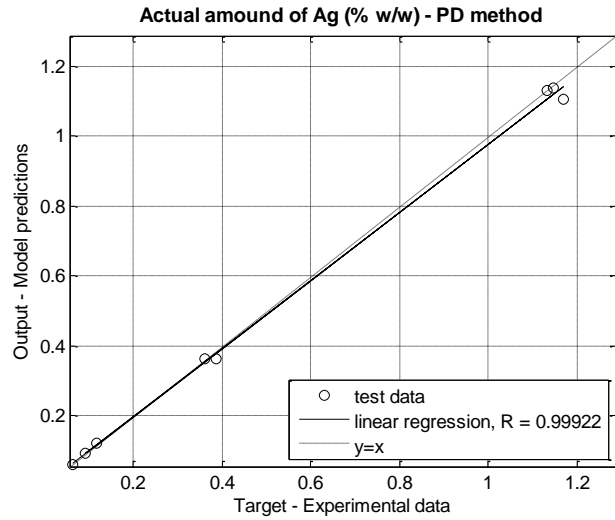
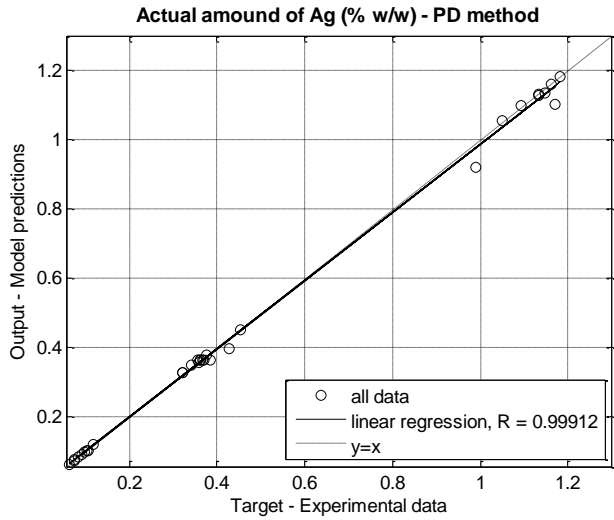
390 **Table 6.** Network topology of the developed models

	Photodeposition – PD	Impregnation – IMP
ANN ₁	3:8:10:1	4:9:8:1
ANN ₂	3:10:10:1	4:8:10:1

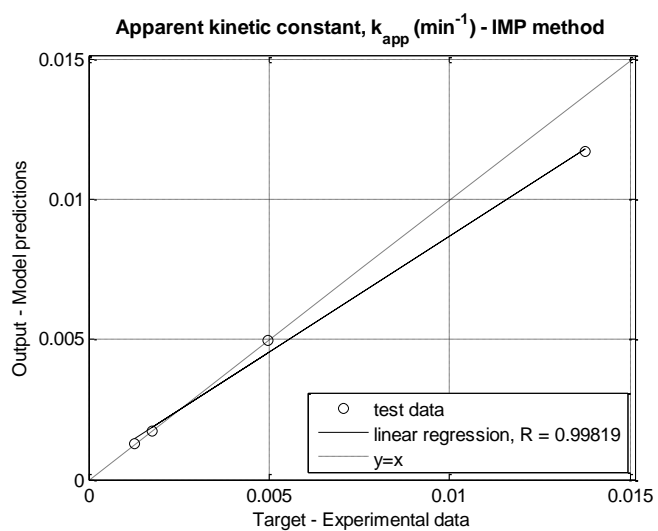
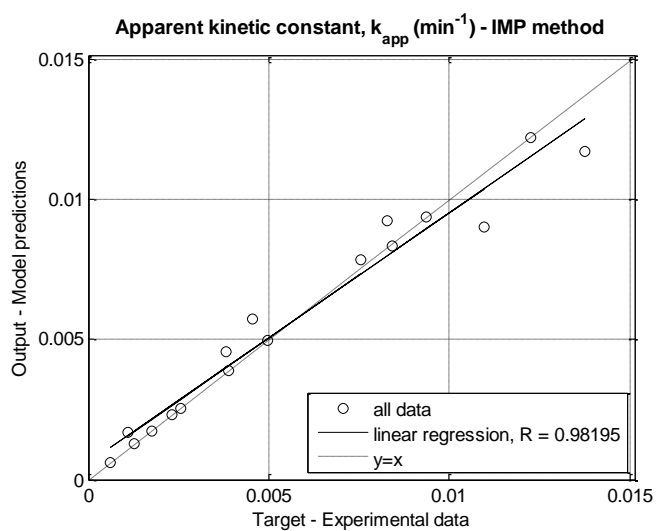
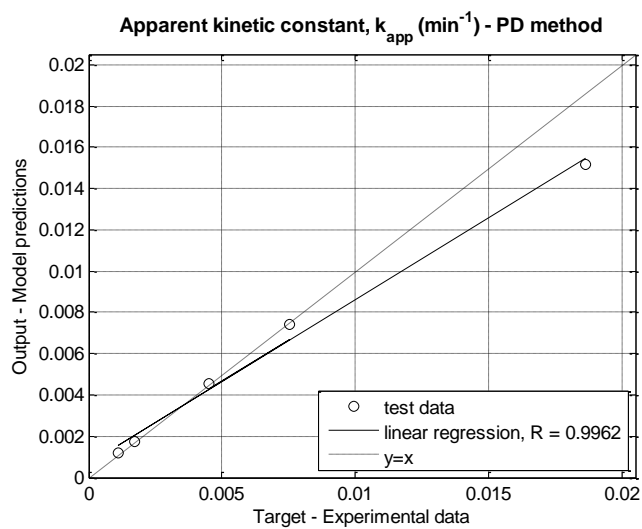
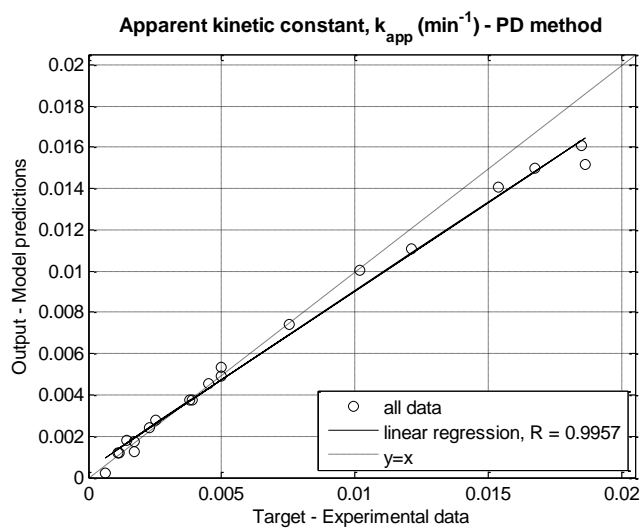
391
 392
 393

394 **3.2 Evaluation of the ANN models**

395 Neural network models are typically assessed, in terms of their accuracy in simulating the
396 experimental data, by plotting the model response with respect to the experimental
397 measurements. A comparison of the points of such plots with the diagonal (i.e., the linear curve
398 corresponding to $y=x$) reveals the accuracy of the developed model. Figures 2 and 3 depict such
399 plots for the ANN₁ and ANN₂ models, respectively. In these plots, the all data and test data sets
400 are shown in order to reveal the accuracy of the model with respect to all available data,
401 including the training data for which a higher accuracy is expected, as well as with respect only
402 to the test data, which represent a subset of the available data that has not been used during
403 the model training process. The value of the correlation coefficient, R, of the linear regression
404 of the data is also shown on the plots. It can be seen that the ANN₁ model exhibits higher
405 accuracy than the ANN₂ model, which seems to under-predict the experimental values at the
406 high-values domain of k_{app} but, in general, remains quite accurate as well. This can be partially
407 attributed to the smaller size of available experimental data for the second model. The values
408 of the experimental data used for the development of the models and the respective model
409 predictions are also given in Tables 4 and 5. Note that, for the training of the models of the
410 photodegradation experiments, ANN₂, the target values of the experimental apparent rate
411 constant were transformed to their log values, in order to avoid a variation over several orders
412 of magnitude. Nevertheless, in all graphical and numerical results presented in this paper, the
413 original non-transformed values are shown for reasons of simplicity.



414 **Figure 2.** Regression plots of the experimental data (all data and test data sets) versus model predicted values for
 415 the developed neural network models ANN₁-PD (top) and ANN₁-IMP (bottom).
 416



417 **Figure 3.** Regression plots of the experimental data (all data and test data sets) versus model predicted values for
 418 the developed neural network models ANN₂-PD (top) and ANN₂-IMP (bottom).
 419

420 **3.3 Analysis of the model results**

421 Once the ANN models have been successfully developed and validated, they can be directly
422 implemented, using input values that do not necessarily correspond to the experimentally
423 tested conditions, in order to assess the effect of the different conditions of each sub-process
424 (i.e., the catalyst synthesis and the degradation tests) to the respective response of interest (i.e.,
425 the actual amount of attached Ag on the photocatalyst and the apparent degradation rate
426 constant, respectively). In this respect, Figures 4a-4f show the effect of pH and actual silver
427 content on the degradation rate of BPA, under different conditions of BPA amount and light
428 wavelength, as produced by the ANN₂-PD model. An initial observation is that the response
429 surfaces are highly irregular, not displaying a clear increasing or decreasing effect. It should be
430 noted at this point that the presented curves can only serve to acquire a general idea about the
431 different trends that the model might display with respect to the variation of certain inputs.
432 They cannot be used to identify specific points or values with accuracy since the viewpoint angle
433 and the graphical interpolation used for their creation may lead to errors.

434 Concerning the effect of pH, it can be seen that, as pH increases the values of k_{app} initially
435 increase, reaching a maximum within the range of pH values 6-9, and then decrease. This effect
436 is particularly obvious in Figures 4d-4f. The pH is an important factor in photocatalysis since it
437 affects the surface charges of both the photocatalyst and the contaminant as follows. In the
438 vicinity above neutral $pH_{pzc}=8.3$ (i.e., value of neutral surface charges for ZnO), hydroxyl-
439 compounds of zinc such as $ZnOH^+$, $Zn(OH)_2$, and $Zn(OH)_3^-$ are formed in the solution and they
440 interact with the undissociated BPA ($HO-C_{15}H_{14}-OH$) toward its oxidation. Below this value, an

441 increase in the hydroxyl ion (OH^-) concentration and, subsequently, to the hydroxyl radical
442 ($\bullet\text{OH}$) concentration leads to the oxidation of BPA. Comparable results have been reported on
443 the degradation efficiency of BPA by pure ZnO by Rahman et al. (2005), who reported 80%
444 degradation efficiency of 100 mg/L of BPA in the pH range of 2 to 8.5, and a significant decrease
445 to 60% at pH 11. Also, Clament Sagaya Selvam et al. (2013) reported the complete degradation
446 of 200 mg/L of BPA at pH 8 and a subsequent decrease of the degradation efficiency at pH
447 values above 9.
448

Figure 4a: BPA = 22 mg/l and UV = 254 nm

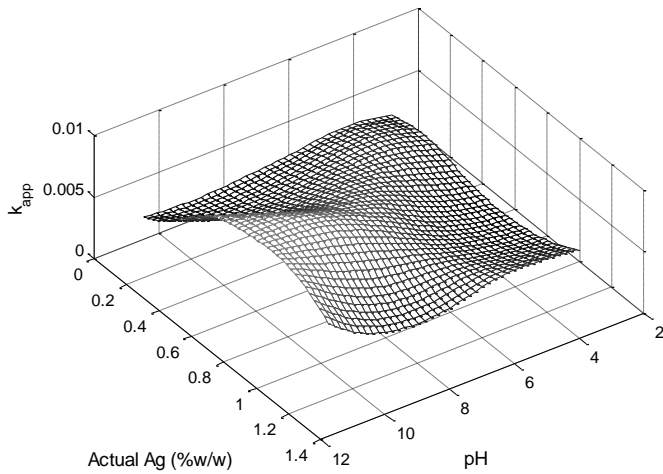


Figure 4b: BPA = 28 mg/l and UV = 254 nm

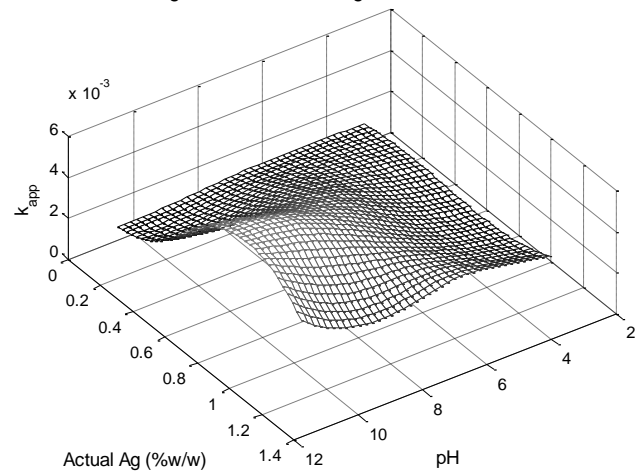


Figure 4c: BPA = 34 mg/l and UV = 254 nm

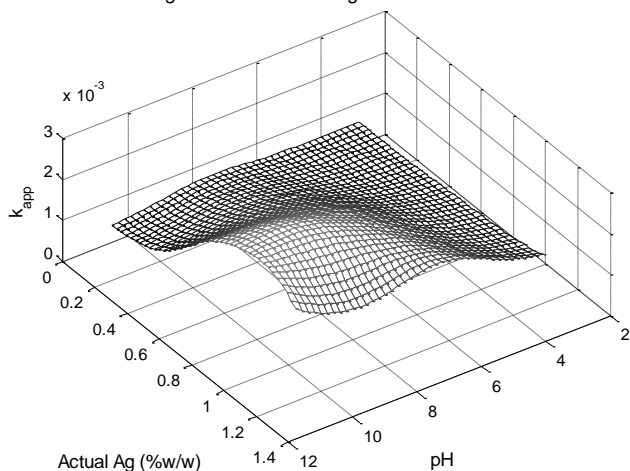


Figure 4d: BPA = 34 mg/l and UV = 302 nm

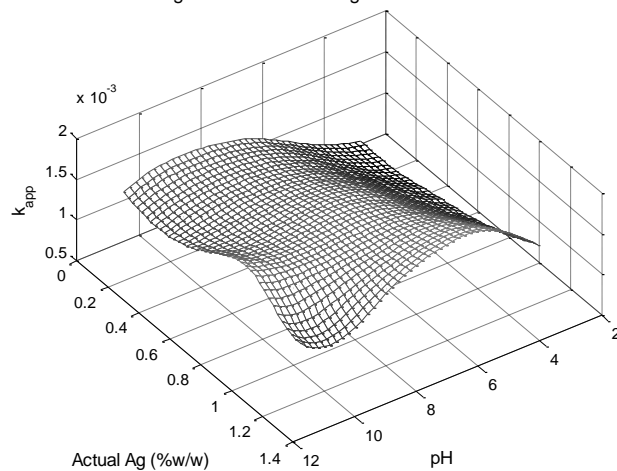


Figure 4e: BPA = 40 mg/l and UV = 254 nm

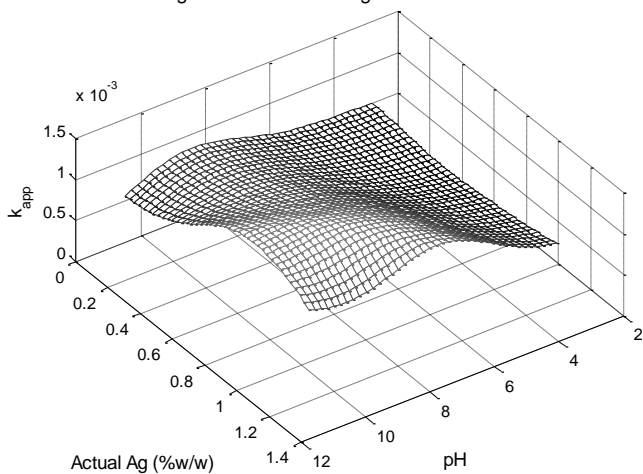
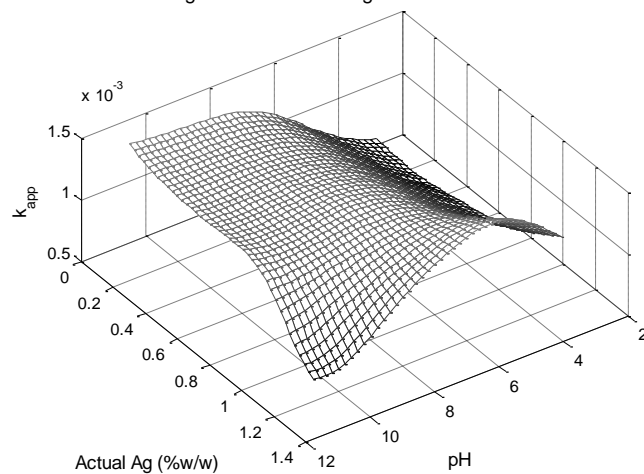


Figure 4f: BPA = 40 mg/l and UV = 302 nm



449 **Figure 4:** Effect of pH and actual silver content (% w/w) on the apparent degradation rate constant under different
450 conditions of BPA content and UV wavelength, as simulated by the ANN₂-PD model.

451 On the other hand, the effects of BPA concentration and UV wavelength are not so evident.

452 Nevertheless, the initial contaminant concentration seems to display an inversely proportional

453 effect on the values of k_{app} , since they seem to be decreasing at higher BPA concentrations. This

454 effect can be partially explained by an absorbance of the UV light (at 255 and 277 nm) by BPA

455 molecules. This way, the activation of the photocatalyst surface is reduced thus producing a

456 *screening effect* of the BPA molecules towards the UV light penetration.

457 A similar effect for all factors can be observed for the impregnation model, ANN₂-IMP, as well.
458 Four representative surfaces are shown in Figures 5a-5d, under different conditions of BPA
459 content and light wavelength. As can be seen, the value of k_{app} displays once more a maximum
460 around the middle of the pH and BPA concentration domains and decreases with increasing BPA
461 concentration.

Figure 5a: BPA = 10 mg/l and UV = 302 nm

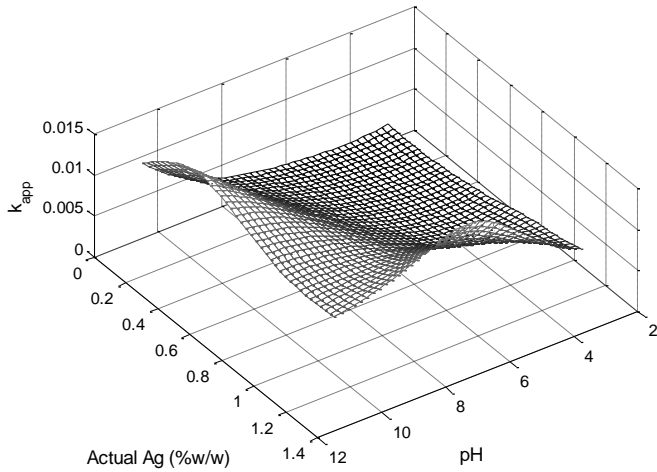


Figure 5b: BPA = 10 mg/l and UV = 365 nm

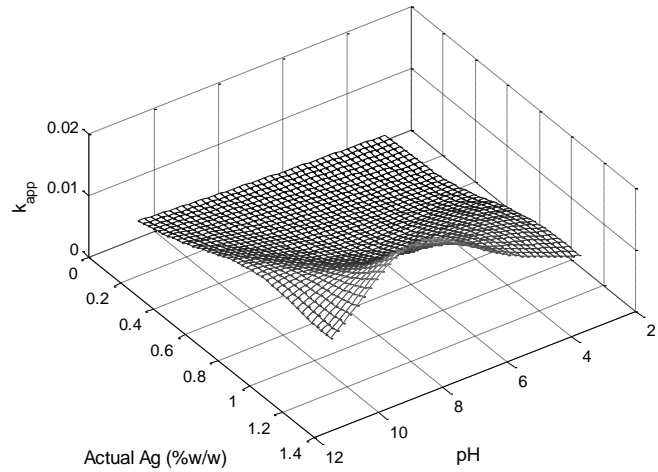


Figure 5c: BPA = 12 mg/l and UV = 302 nm

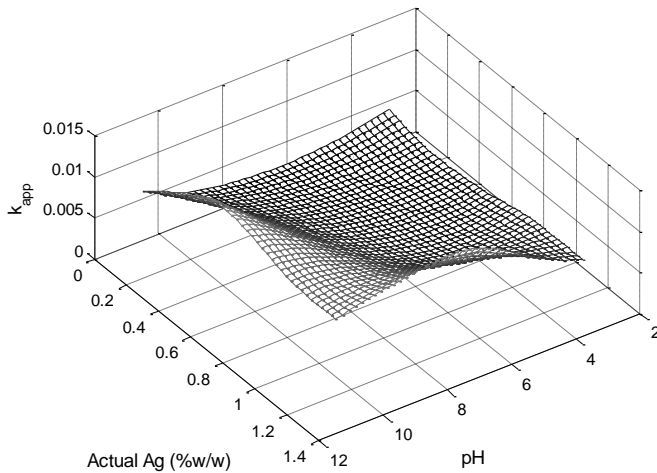
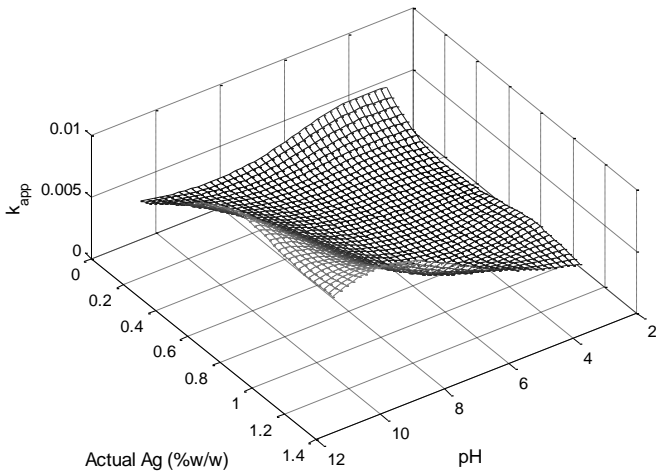


Figure 5d: BPA = 14 mg/l and UV = 302 nm



462 **Figure 5:** Effect of pH and actual silver content (% w/w) on the apparent degradation rate constant under different
463 conditions of BPA content and UV wavelength, as simulated by the ANN₂-IMP model.

464 Concerning the first model, ANN₁, a similar analysis can be made on the effects of the catalyst
465 synthesis conditions on the overall functionalization degree, FD, defined as the ratio of the
466 actual amount of silver on the catalyst particles over the nominal amount of silver used during
467 the catalyst synthesis. In Figures 6a and 6b, two surface plots, similar to the ones previously
468 depicted for ANN₂, are shown corresponding to the photodeposition method and to two
469 different values of nominal amount of silver. The corresponding plots for the impregnation
470 method are depicted in Figures 6c and 6d. As can be seen, there is no significant variation of FD
471 with respect to pH and time when the photodeposition method is implemented. On the other
472 hand, the reaction time seems to have an overall positive effect on the FD values and to display
473 a maximum around 150 min, when the impregnation method is used.

474 The effect of pH seems to vary with the time of reaction and the nominal AG amount, especially
475 for the photodeposition method. At the same time, an excess nominal amount of silver does not
476 seem to display a positive effect on the functionalization degree when the impregnation
477 method is implemented, which is particularly obvious in Figure 6d. It should be noted at this
478 point that the experimental values of FD that are higher than 1 are due to experimental
479 sampling and titration errors, as explained in (Jasso-Salcedo et al., 2014). As a consequence it is
480 normal that the developed neural network model, which was trained on the basis of these
481 experimental values, provides responses that result in values of FD higher than 1.

Figure 6a: Nominal Ag amount = 0.24373 %w/w

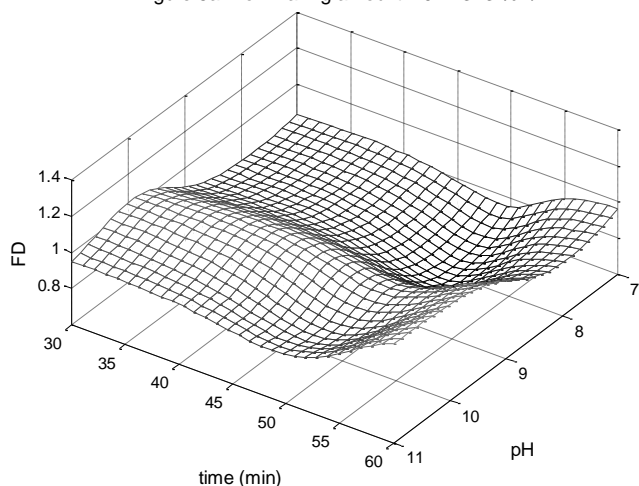


Figure 6b: Nominal Ag amount = 0.92587 %w/w

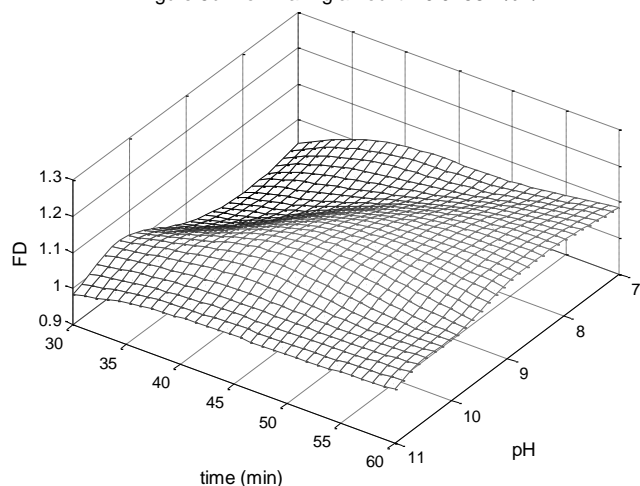


Figure 6c: Nominal Ag amount = 0.81974 %w/w

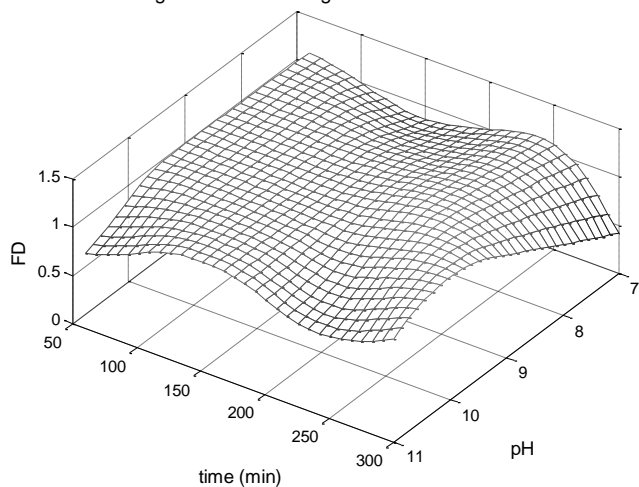
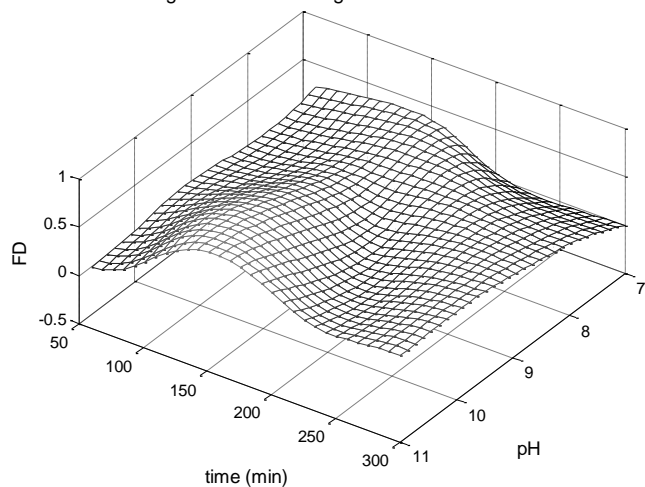


Figure 6d: Nominal Ag amount = 4.3825 %w/w



482 **Figure 6:** Effect of pH and nominal silver content (% w/w) on the functionalization degree (i.e., the ratio of actual to
483 nominal amount of Ag) under different values of nominal Ag amount as simulated by the ANN₁-PD (a, b) and ANN₁-
484 IMP (d, c) models.

485

486 **3.4 Optimization step 1 - apparent kinetic rate constant, k_{app}**

487 Given the nature of the photodegradation process and the definition of the output of the

488 process on the basis of the apparent kinetic rate constant of a first-order degradation reaction,

489 it becomes evident that the desired value of this constant is the maximal possible value it could

490 attain, as this will lead to a faster degradation of a maximum amount of BPA. Hence, the first
 491 step of the optimization study, on the basis of ANN₂, was the solution of a maximization
 492 problem in terms of the conditions of the photodegradation process, namely the actual amount
 493 of attached AgNPs, the pH, the BPA concentration and the light wavelength. The deployment of
 494 an EA for the solution of this problem for both methods of photocatalyst synthesis resulted in
 495 the sets of optimal conditions shown in Table 7. Note that, for the EA algorithm, the following
 496 parameters were used: the size of the population was set to 1000 individuals, the survival rate
 497 was set to 70% and the mutation rate to 10%. The program was entirely written and run on
 498 MATLAB (version 8.3.0.532; academic license) while the convergence of the algorithm was
 499 tested in terms of a tolerance in the relative difference between the best and worst criterion
 500 values of each generation, set in the order of 1%. The CPU time required for every optimization
 501 run was in the order of 30 s on a 2x2.4 GHz Intel® Xeon® Workstation.

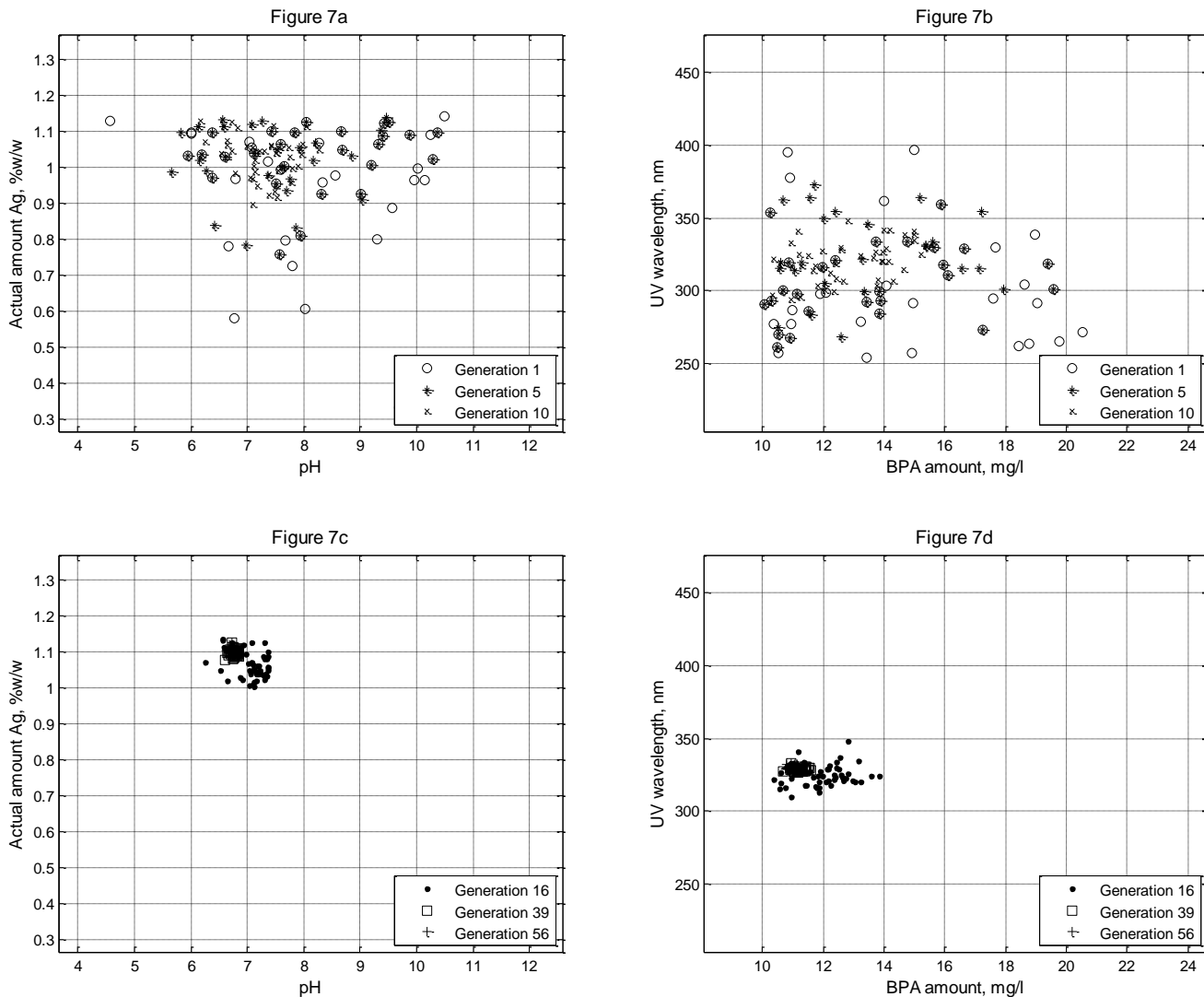
502

503 **Table 7:** Results of the first optimization step on the maximization of k_{app}

Optimal photodegradation conditions for the photodeposition method ($k_{app,max} = 0.0383 \text{ min}^{-1}$)			
Actual amount Ag, %w/w	pH (initial value)	BPA concentration, mg/L	Wavelength, nm
1.10	6.7	10.8	330
Optimal photodegradation conditions for the impregnation method ($k_{app,max} = 0.0167 \text{ min}^{-1}$)			
Actual amount Ag, %w/w	pH (initial value)	BPA concentration, mg/L	Wavelength, nm
0.78	10.1	10.2	358

504

505 In order to follow the evolution of the optimization and to verify its convergence around one (or
 506 more) optimal(s), one can plot the positions of a number of 'best' (i.e., top ranked) individuals,
 507 corresponding to an equal number of optimal conditions, along different generations of the
 508 optimization procedure. In Figures 7a-7d, a set of 50 optimal conditions is depicted, as
 509 calculated by the EA optimization of the ANN₂-PD model.



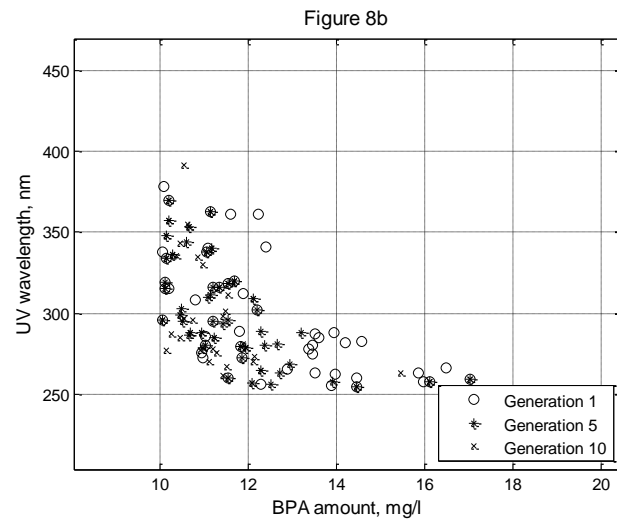
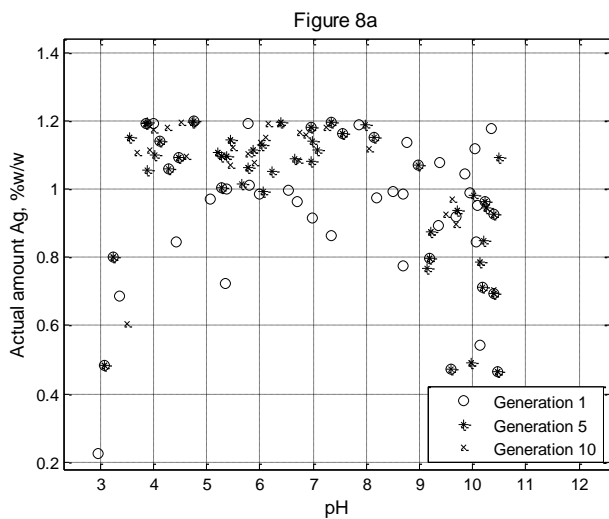
511 **Figure 7:** Presentation of the 50 optimal conditions in terms of the actual amount of Ag and pH (a, c) and the UV
 512 wavelength and the BPA amount (b, d), as predicted by the EA optimization on the basis of the ANN₂-PD model
 513 after 1, 5 and 10 generations (a, b) as well as after 16, 39 and 56 generations (c, d).

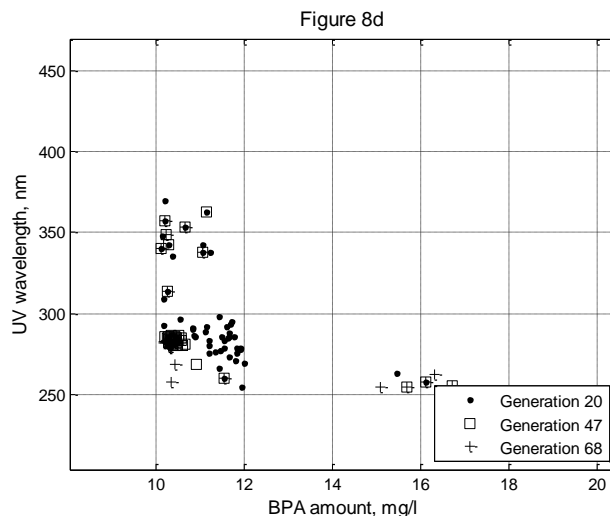
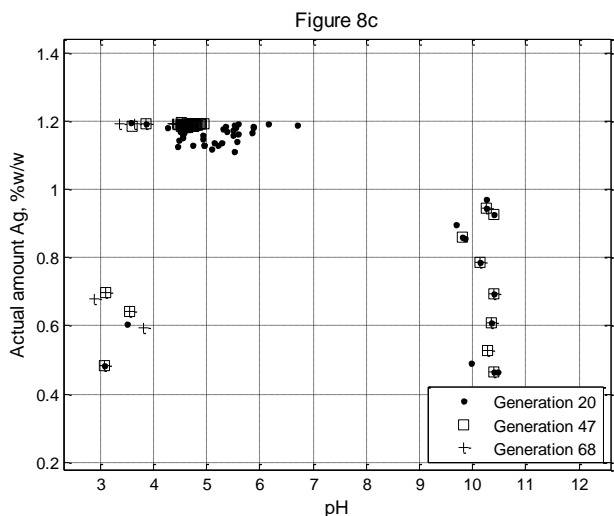
514 Since there are four different factors for this model, two plots are produced for each
 515 generation, one corresponding to the optimal values of the actual amount of silver and pH and
 516 another corresponding to the optimal values of the UV wavelength and the initial BPA amount.
 517 The same Figures have been plotted for three different generations at the early stages of the
 518 optimization (i.e., generations 1, 2 and 10, cf. Figures 7a and 7b) as well as for three generations

519 at the middle and final stages of the optimization (i.e., generations 16, 39 and 56, cf. Figures 7c
520 and 7d). This illustration reveals the convergence of the optimization around a unique set of
521 optimal conditions (cf. Table 7). In this specific case, the convergence was achieved after 56
522 iterations, according to the convergence criterion defined earlier in this Section. Note that the
523 predicted optimal value of k_{app} is significantly increased with respect to the experimentally
524 measured values.

525 Figures 8a-8d present the corresponding plots of the same optimization problem but for the
526 impregnation method (i.e., on the basis of ANN₂-IMP). In this case, several local maxima seem to
527 exist so the optimization does not converge around one single set of optimal conditions. The
528 conditions reported in Table 7 are the ones that lead to the maximum attain value of the
529 apparent rate constant and correspond to the set of points located on the right in Figure 8c and
530 on the top left in Figure 8d. In any case, this method seems to lead to significantly lower optimal
531 values of the rate constant, in comparison to the photodeposition method.

532





533 **Figure 8:** Presentation of the 50 optimal conditions in terms of the actual amount of Ag and pH (a, c) and the UV
 534 wavelength and the BPA amount (b, d), as predicted by the EA optimization on the basis of the ANN₂-IMP model
 535 after 1, 5 and 10 generations (a, b) as well as after 20, 47 and 68 generations (c, d).

536

537 **3.5 Optimization step 2 - actual amount of silver in the ZnO photocatalyst**

538 On the basis of the optimal amount of AgNPs defined by the previous optimization step, a
 539 second optimization run was carried out in order to define the conditions that would result in
 540 the synthesis of a photocatalyst with this optimal amount of silver nanoparticles. So, in this
 541 case, the goal was to minimize the objective function defined by the absolute difference
 542 between the model response (i.e., the actual Ag amount) and the desired Ag amount, as this
 543 was defined in the previous optimization step. This second step of the optimization study was
 544 based on ANN₁ and the results of the EA that was deployed for the solution of this problem are
 545 shown in Table 8. In both cases, the error between the desired and attained value was inferior
 546 to 0.01%, significantly lower than the associated experimental error of the measurements.

547

548

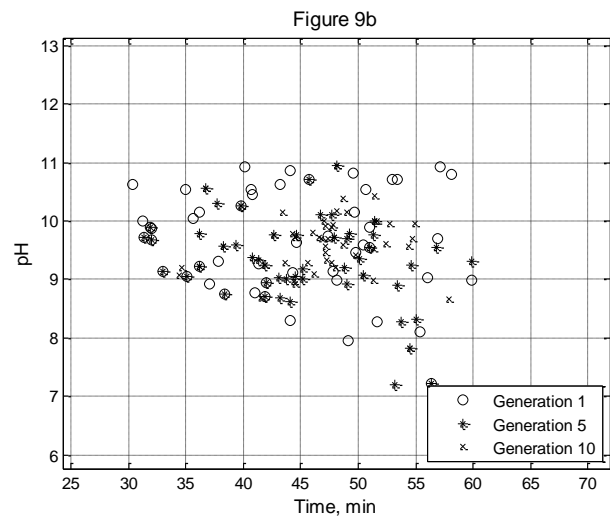
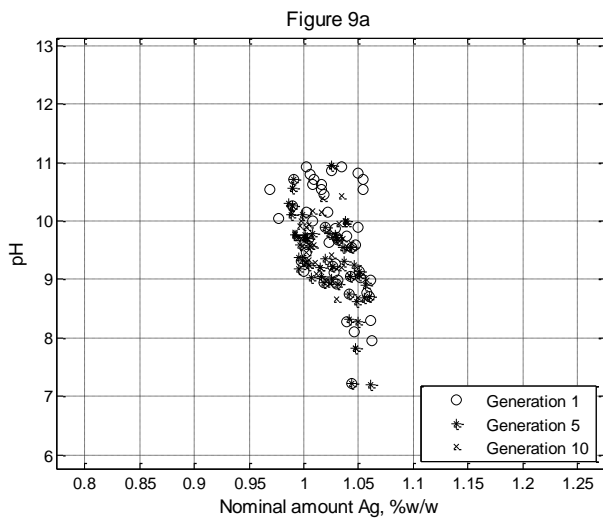
549

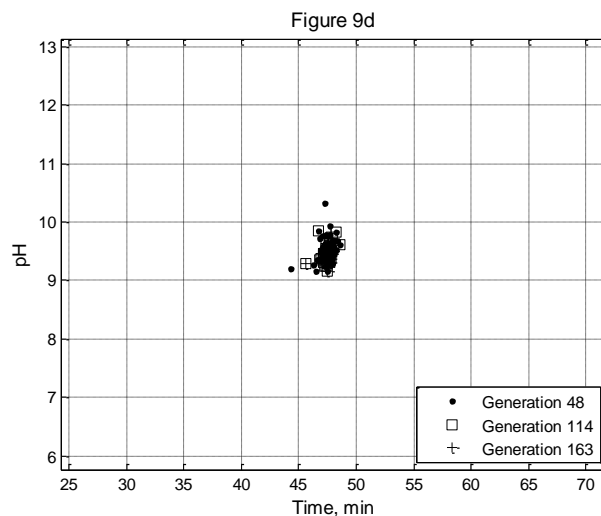
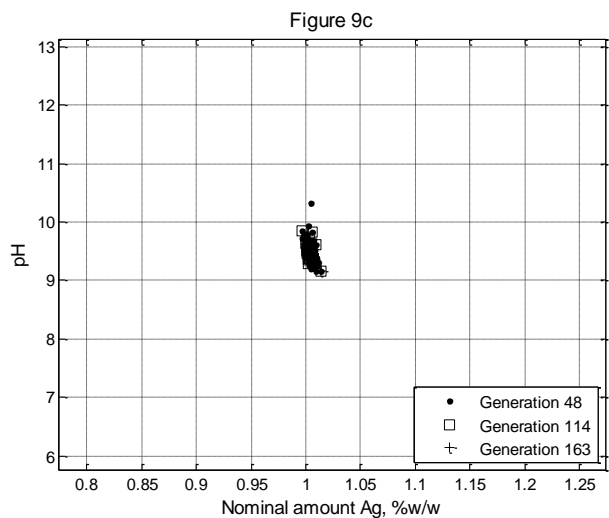
550 **Table 8:** Results of the 2nd optimization step on the synthesis of a photocatalyst with a desired content of AgNPs
Optimal photocatalyst synthesis conditions for the photodeposition method (Actual Ag %w/w = 1.10)

Nominal amount Ag, %w/w	pH	Time, min
<i>1.00</i>	<i>9.5</i>	<i>48</i>
Optimal photocatalyst synthesis conditions for the impregnation method (Actual Ag %w/w = 0.78)		
Nominal amount Ag, %w/w	pH	Time, min
<i>0.69</i>	<i>8.5</i>	<i>214</i>

551

552 The respective 2D plots of the evolution of the 50 optimal conditions in terms of the model
553 factors are presented in Figures 9a-9d and 10a-10d, for the photodeposition and the
554 impregnation methods respectively. Note that, as the number of factors is limited to three in
555 this case, both couples that are used in the plots contain pH as one of the factors.

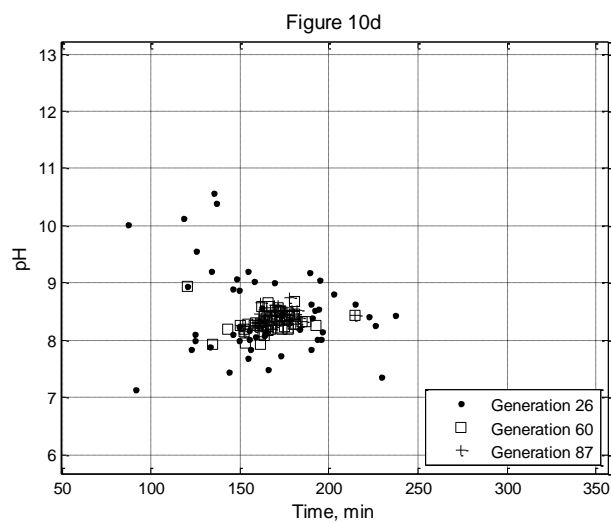
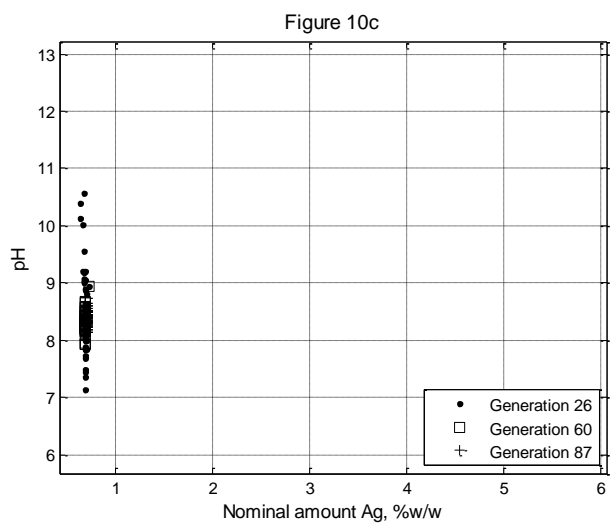
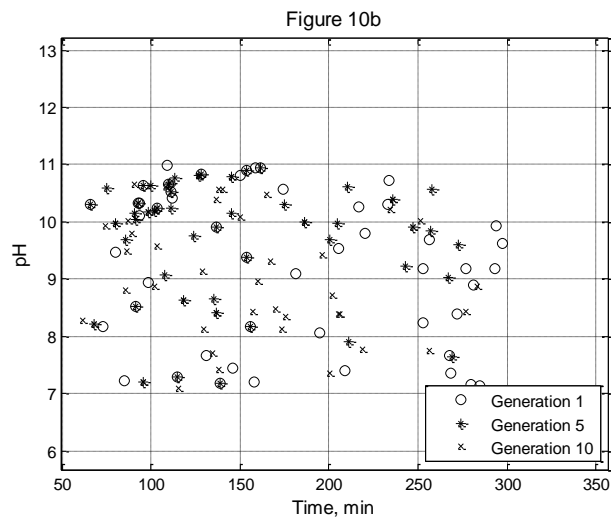
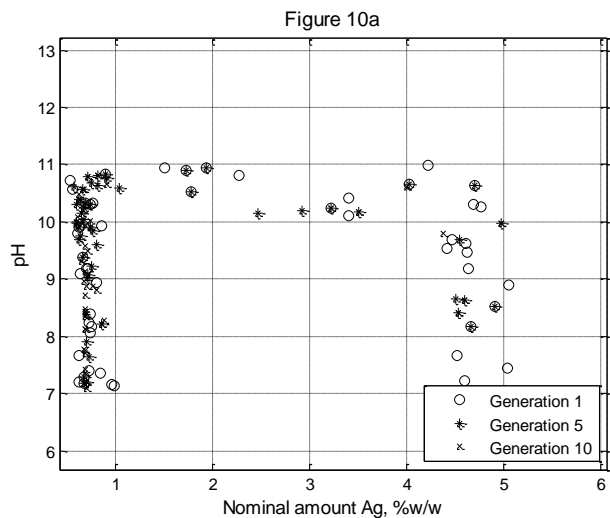




556 **Figure 9:** Presentation of the 50 optimal conditions in terms of the nominal amount of Ag and pH (a, c) and the
 557 reaction time and pH (b, d), as predicted by the EA optimization on the basis of the ANN₁-PD model after 1, 5 and
 558 10 generations (a, b) as well as after 48, 114 and 163 generations (c, d).

559 The results of these optimization runs are quite similar to the first optimization runs as, once
 560 again, the impregnation method seems to provide several alternatives as local minima,
 561 especially in terms of the value of the pH, as becomes evident in Figures 10a and 10c. The
 562 photodeposition method, on the other hand, has a clear minimum of the objective function that
 563 is identified by the EA algorithm already somewhere between the 10th and 48th iteration,
 564 despite the fact that the algorithm requires more than 160 iterations to meet the convergence
 565 criterion. Finally, a paradox is observed in both optimization results since the optimal nominal
 566 amount of Ag is lower than the desired actual amount of Ag. Once again, this is due to the fact
 567 that the models have been trained with experimental data containing such discrepancies, which
 568 are caused by the experimental error associated with the experimental protocol and the
 569 analytical method (Jasso-Salcedo et al., 2014). This should not be interpreted as an error
 570 associated with the modeling framework or the optimization approach.

571



572 **Figure 10:** Presentation of the 50 optimal conditions in terms of the nominal amount of Ag and pH (a, c) and the
 573 reaction time and pH (b, d), as predicted by the EA optimization on the basis of the ANN₁-IMP model after 1, 5 and
 574 10 generations (a, b) as well as after 26, 60 and 87 generations (c, d).

575

576 4 Conclusions

577 In the present work, a modeling framework on the basis of Artificial Neural Networks was
 578 presented for the simulation of the effects of two important stages of a photocatalytic process,
 579 namely the catalyst synthesis and the photodegradation experiments, on the final

580 photodegradation performance of the synthesized photocatalyst. In this respect, a two-stage
581 ANN model was developed, connected by means of introducing the response of the first model
582 as a factor to the second model. The developed models were subsequently introduced in an
583 optimization study, carried out with the aid of an evolutionary algorithm and comprised also of
584 two steps. Through this integrated approach, it has been possible to study simultaneously the
585 effects of a series of important conditions associated with two totally distinct stages of the
586 process and to connect the initial photocatalyst synthesis conditions with its final
587 photodegradation performance.

588 By means of the developed models, the effects of pH, nominal amount of silver nanoparticles
589 introduced in the suspension and reaction time were assessed in terms of their effects on the
590 actual amount of silver nanoparticles that are finally retained on the ZnO surface. At the same
591 time, this amount of attached silver along with the pH, the light wavelength and the initial
592 contaminant amount present in the photodegradation experiments were studied in terms of
593 their effect on the photodegradation performance of the synthesized photocatalyst. This
594 performance was associated with an apparent rate constant, thus eliminating the time from the
595 factors of the photodegradation tests.

596 The decoupling of these two processes that was proposed in this study allowed a better
597 understanding of the nature of the indisputable indirect bond that exists between them. In this
598 respect, it has been shown that an intermediate quality criterion of the photocatalyst, namely
599 the actual amount of silver attached to the ZnO surface that, in turn, can only be controlled by
600 the photocatalyst synthesis conditions, displays a direct effect on its photodegradation
601 performance. Finally, by investigating two different methods of the photocatalyst synthesis,

602 namely a photodeposition and an impregnation method, the study has also demonstrated that
603 it can display an important effect on the final photodegradation efficiency of the photocatalyst.

604

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Supplementary material

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Modeling and Optimization of a photocatalytic process: Degradation of

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endocrine disruptor compounds by Ag/ZnO

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784 **Table S1.** MSE values corresponding to different network topologies of the developed models

ANN ₁ - PD					ANN ₁ - IMP				
Topology	MSE All	MSE Train	MSE Val	MSE Test	Topology	MSE All	MSE Train	MSE Val	MSE Test
8:10	5.13E-05	7.42E-05	1.98E-14	1.99E-06	10:10	2.40E-03	2.84E-03	2.74E-03	1.22E-04
7:8	5.80E-05	8.11E-05	8.43E-06	6.05E-06	6:10	2.41E-03	3.27E-03	9.80E-04	4.02E-05
9:8	8.25E-05	9.69E-05	7.84E-05	2.29E-05	10:3	2.42E-03	3.46E-03	2.17E-04	6.83E-05
5:4	1.35E-04	1.28E-04	2.69E-05	2.76E-04	9:6	2.49E-03	3.24E-03	1.22E-03	4.11E-04
8:3	1.38E-04	1.42E-04	1.86E-04	7.11E-05	9:2	2.52E-03	2.77E-03	1.41E-04	3.79E-03
4:9	1.50E-04	7.27E-05	6.27E-04	1.15E-05	7:5	2.63E-03	1.05E-05	2.76E-05	1.67E-02
3:8	1.87E-04	2.22E-04	5.66E-05	1.68E-04	3:5	2.66E-03	3.46E-03	8.28E-04	9.82E-04
10:3	1.93E-04	1.71E-04	4.13E-04	7.12E-05	5:1	2.70E-03	3.85E-03	2.16E-04	1.12E-04
7:1	1.99E-04	2.57E-04	9.56E-05	4.97E-05	9:9	2.71E-03	3.93E-03	1.58E-06	6.00E-05
8:5	2.29E-04	5.57E-05	3.80E-05	1.18E-03	6:2	2.74E-03	1.28E-03	1.17E-02	1.82E-04
ANN ₂ - PD					ANN ₂ - IMP				
Topology	MSE All	MSE Train	MSE Val	MSE Test	Topology	MSE All	MSE Train	MSE Val	MSE Test
9:8	1.56E-04	1.63E-04	1.11E-04	1.68E-04	8:10	1.10E-04	1.69E-04	2.79E-11	8.81E-11
17	4.39E-04	5.34E-04	7.90E-06	3.64E-04	3:10	1.39E-04	2.15E-04	3.14E-08	1.10E-08
8:8	6.33E-04	7.28E-04	6.62E-04	9.73E-05	8:4	1.50E-04	1.23E-04	4.01E-04	1.48E-08
4:9	8.32E-04	4.15E-04	2.48E-03	1.40E-03	11	2.06E-04	1.28E-06	2.16E-06	1.16E-03
4:7	1.04E-03	9.44E-04	9.74E-07	2.59E-03	8:7	5.45E-04	7.42E-04	6.20E-05	3.05E-04
14	1.18E-03	1.15E-03	7.75E-05	2.46E-03	9:4	8.41E-04	6.31E-04	3.32E-19	2.45E-03
15	1.19E-03	1.60E-03	2.83E-07	1.71E-04	9:10	1.20E-03	5.95E-05	2.58E-04	6.33E-03
8:10	1.22E-03	1.37E-03	8.44E-04	7.48E-04	10:1	1.25E-03	1.80E-03	2.44E-04	2.67E-04
16	1.38E-03	1.76E-03	6.10E-04	9.68E-05	5:10	1.33E-03	2.01E-03	1.46E-04	3.38E-05
3:7	1.48E-03	2.01E-03	1.22E-04	5.52E-05	16	1.42E-03	2.17E-03	1.49E-05	4.78E-05

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