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A New Catalytic System for the Photodegradation of Endocrinal Disruptors: Synthesis and Efficiency Modeling and Optimization

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Nowadays, the challenge of understanding relationships between catalysts properties and performance in the context of heterogeneous catalysis is a hot topic. Indeed, catalytic processes are generally affected by many different operational parameters that need to be modeled and optimized. The challenge can be addressed using artificial neural networks due to their flexibility to work without mathematical description of the process. The present work enters within the framework of the photodegradation of water contaminants using ZnO-based catalysts. ZnO is a non-toxic cheap material with an interesting photocatalytic potential. However, its application is reduced because of its poor efficiency, photocorrosion and difficulties for recovery. The objective of this work is to improve this efficiency, regarding particularly the photodegradation of an endocrinal disruptor: bisphenol-A (BPA), via the synthesis of a new catalytic system based on ZnO and the modeling of both the synthesis process and photocatalytic performance of this new catalytic system. Modeling and optimization will be carried out using artificial neural network tools coupled to an evolutionary algorithm. The connection between the two artificial neural network models will make it possible to identify the optimal synthesis parameters that lead to the maximum photocatalytic efficiency (within the studied domain), thus shedding light on the association of the system structure with its photocatalytic performance.

1. Introduction

Modeling tools like artificial neural networks (ANNs) have drawn the attention in the field of heterogeneous catalysis for water treatment in the past ten years but found only recently application in modeling the structure-performance relationships. ANNs have been sufficiently capable to model the complex nonlinear relationships between input variables (experimental operational parameters) and output criteria (responses) of complex processes (Osulale and Zhang, 2014). In recent years, modeling of photocatalyst doping and photocatalytic activity using ANNs has become a trend (Antonopoulou and Konstantinou, 2013), with a total of 34 publications appearing after a simple literature search under the string: “photocatalysis AND artificial neural network”, corresponding to the period 1991-2014. Most of them were published in the research area of engineering, chemistry and environmental science, which seems logic since this type of modeling approach can be extended to the industry to generate engineered products and reduce the cost of the optimized design. The optimization of the photocatalytic performance of a new catalytic system gains importance mainly when it has to be used at industrial scale. In this case, the cost becomes a decisive factor in the competition with well-known photocatalysts (e.g., TiO_2). In this respect, a novel modeling approach is proposed in this work, making use of two different ANN models in order to correlate the synthesis parameters of the catalyst with its photocatalytic performance on the degradation of a contaminant with endocrine disruption properties:

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bisphenol-A (BPA). More specifically, the present study will involve the modeling of (i) the functionalization of ZnO with silver nanoparticles, giving rise to a new catalytic system (Ag/ZnO) and (ii) the photodegradation of BPA in aqueous solutions using this system. This novel two-step modeling approach, on the basis of multi-layer back-propagating neural networks, will be coupled to an evolutionary algorithm (Viennet et al., 1996,) to carry out an inverse optimization that makes it possible to finally correlate the synthesis conditions with the photocatalytic performance of Ag/ZnO.

2. Experimental section

2.1 Materials

Zinc oxide particles (average pore diameter: 216.63 nm) and Silver nanoparticles, (average crystallites size:7 nm) were provided by Degussa Co. and CIDT-Penoles, Mexico respectively. HCl (38 %), NaOH, Ethanol and Bisphenol-A (2,2-bis(4-hydroxyphenyl)propane)) (>99 %), were purchased from Sigma-Aldrich (St. Louis, USA). All reagents were used as received.

2.2 Synthesis and characterization of the catalytic system Ag/ZnO

The catalytic system Ag/ZnO was prepared by two methods: photodeposition (PD) and impregnation (IMP) (Jasso-Salcedo et al., 2014). In both methods, a suspension containing ZnO and stabilized silver nanoparticles (AgNPs) was adjusted at desired initial pH values, using either 0.1N HCl or 0.5N NaOH below and above the pH point of zero charge of ZnO nanoagglomerates (pH_{PZC} = 8.2). The suspension was stirred during a certain time and then the recovered solids were submitted to centrifugation/re-dispersion cycles in H_2O:EtOH to remove the non-attached AgNPs from the ZnO surface. Photodeposited samples were irradiated (250 nm, 3.4 mW/cm^2) under stirring during different times, recovered, washed, dried (80 °C, 8 h) and stored in darkness. Impregnated samples were only stirred, recovered, washed, dried (80 °C, 8 h) and calcined at 300 °C for 1 h before storage. The resulting samples were characterized using inductively coupled plasma optical emission spectroscopy, X-ray diffraction, scanning and transmission electron microscopy, nitrogen adsorption-desorption, Fourier transform infrared spectroscopy and UV-Visible spectroscopy. These analyses clearly demonstrated that the two-functionalization methods promoted homogeneous distribution of AgNPs on ZnO catalyst. They also showed that, in the case of the photodeposition method, the UV irradiation ensures strong interactions between Ag and ZnO. Moreover, in this case, an increase in lattice parameters and a decrease in BET surface area were observed, indicating insertion of Ag^+ ions into the crystalline structure and between the pores of ZnO, respectively.

2.3 Photodegradation of bisphenol-A

Aqueous suspensions of BPA and the photocatalyst were placed in a glass container. Prior to irradiation, the suspension was mechanically stirred for 10 min in darkness. Then it was irradiated by UV light at different possible wavelengths, namely at 254, 302 or 365 nm using a UV lamp (3UV-38, UVP Inc.) or at 450 nm using a fluorescent lamp (F8T5/CW, Hampton Bay), placed at 8 cm from the top of the solution. The experiments were carried out at room temperature (20±1 °C) without external oxygen supply. Samples were then collected at regular time intervals and centrifuged at 3,000 rpm for 10 min to recover the photocatalyst powder. The liquid samples were filtered (0.45 µm) before analysis. The irradiation time evolution of the concentration of residual BPA was determined by HPLC, which allowed evaluating the effect of the wavelength, initial pH and amount of photocatalyst on the photodegradation of BPA. For example, Figure 1 shows the effect of the wavelength and allows comparing the efficiency of pure ZnO, Ag/ZnO-PD and Ag/znO-IMP.

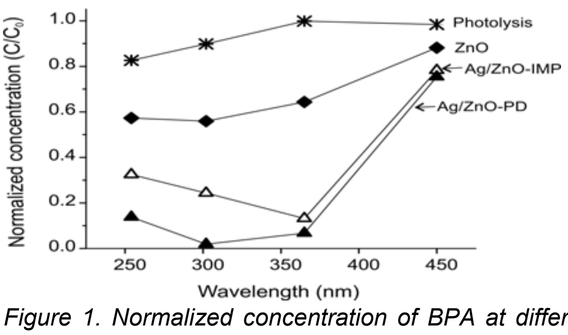

Figure 1. Normalized concentration of BPA at different wavelengths using ZnO and Ag/ZnO photocatalysts (test conditions: BPA=10 mg/L, photocatalyst = 1 g/L, pH=10.5, reaction time = 120 min under λ = 254, 302, 365 nm, and 180 min under λ>450 nm).

3. ANN modeling and optimization of the catalytic system

3.1 Definition of the model input/output

Model A: synthesis of ZnO. The independent variables, namely nominal AgNPs amount, pH and time, and their respective ranges of variation were selected on the basis of the literature (Amadelli et al., 2008). The actual amount of AgNPs attached to the ZnO surface, defined by Eq(1), was selected as the response of the model:

$$Ag\ \%\ w/w = [(Ag)/(Ag + Zn)]*100 \tag{1}$$

The masses of Ag and Zn were obtained from elemental quantification using inductively coupled plasma spectrometry at 328 nm and 213.9 nm.

Model B: photocatalytic activity (apparent rate constant). The independent variables of this model were pH, BPA concentration, wavelength and actual AgNPs amount (i.e., the output of model A). The response was chosen to be the apparent rate constant (k_{app}) of BPA degradation which was obtained according to the following treatment: the concentration (C) versus time (t) plots (i.e., the overall degradation curves) was approximated by a first-order exponential decay function given in Eq(2), that best fitted the actual data.

$$C = a\ exp^{bt} \tag{2}$$

The derivation of the exponential regression function has a more “physical sense” using the typical kinetic behavior of Eq(3), where r is the degradation rate, k_{app} the apparent rate constant, C the concentration of BPA at each time and n the reaction order.

$$dC/dt = (a\ exp^{bt})\ b = r = k_{app}\ C^n \tag{3}$$

The assumed first-order kinetics behavior of the process (i.e., n = 1) was verified by a plot of lnr versus lnC (Figure 2) for each experiment. Via this treatment, the experimental values of k_{app} were also evaluated. Note that the implementation of a regression technique to describe the complete degradation curve provides a more global approach on the photodegradation performance optimization problem, which does not include time in the factors of the experiment.

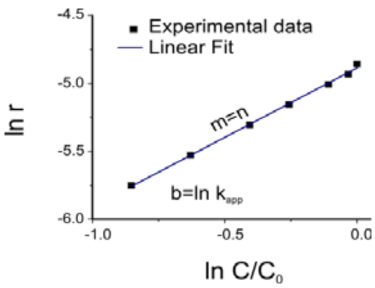

Figure 2: Linear plot Y=mX + b to obtain the kinetic parameters (k_{app} and n).

3.2 Experimental design

A central composite design was used for the functionalization of ZnO by PD and IMP methods. The experimental ranges of variation of the independent variables are shown in Table 1. A total of 27 experiments per synthesis method were used to feed Model A. On the other hand, a total of 20 photodegradation experiments per method at arbitrary conditions (Table 2) were used for the tuning of Model B.

Table 1: Experimental ranges of the independent variables of CCD design for each functionalization method

Variables	Signification	Range for PD	Range for IMP
INPUT			
X_1	AgNPs nominal amount (%w/w)	0.1-1	0.1-5
X_2	Initial pH	7-11	7-11
X_3	Time (h)	0.5-1	2-5
OUTPUT			
Y	AgNPs actual amount (%w/w)		

Table 2: Experimental range of the independent variables for the photocatalytic tests

Variables	Signification	Range
INPUT		
W_1	Initial pH	2.8-10.5
W_2	AgNPs actual amount (%w/w)	0-1.2
W_3	BPA (mg/L)	10-40
W_4	Wavelength (nm)	254,302,365,450
OUTPUT		
Z	k_{app} (min^{-1})	

3.2 Artificial neural network model

A feed-forward three-layered perceptron network was used. The experimental data were randomly divided into training, validation and test subsets (70 %, 15 % and 15 %). The structure denoted as (In:Hid:Out) corresponds to the numbers of neurons in the input, hidden and output layers, respectively. The number of neurons in the hidden layer was selected based on the correlation coefficient (R^2) and the mean squared error (MSE) of the training and validation sets. The Neural Network Toolbox of the commercial software package MATLAB 7.11.0 (academic license) was adapted to the case study.

3.3 Optimization by evolutionary algorithm

The ANN models were coupled with an evolutionary algorithm (EA) in terms of a consecutive two-step mono-objective optimization of two separate objective functions. The first step maximized the objective function defined by Eq(4), using Model B, to obtain an optimal value for the actual amount of AgNPs. At the second step, the difference of the actual amount of AgNPs with this optimal amount was set as the new objective function, defined by Eq(5), that was minimized in terms of Model A. As a result, the conditions of Ag/ZnO synthesis (i.e., Ag NPs nominal amount, pH and reaction time) that maximize the photocatalytic degradation of BPA, were identified.

$$Z_{opt} = \max(Z)\Big|_{W_{1,opt},W_{2,opt},W_{3,opt},W_{4,opt}} \tag{4}$$

$$Y_{opt} = \min\left(Y - W_{2,opt}\right)^2\Big|_{X_{1,opt},X_{2,opt},X_{3,opt}} \tag{5}$$

4. Results and Discussion

4.1 ANN modeling of the photocatalytic system

Figure 3A shows the correlation of the experimental and predicted data values for the synthesis of the catalytic system and their performance. R^2 and MSE confirm a good agreement of the ANN model with the experimental data for both functionalization methods. The results show that ANNs can adequately model and predict the whole photocatalytic system in the experimental range tested in this work.
Figure 3B shows a very good agreement between predicted and experimental data of the kinetic parameter k_{app}. ANN models correlate with good accuracy the experimental conditions (i.e. pH, AgNPs content, BPA concentration and wavelength).
Moreover, the validation experiments clearly confirm that the catalytic system Ag/ZnO-PD is more efficient than Ag/ZnO-IMP. To our knowledge, this is the first time that an apparent degradation rate constant (k_{app}) is used as response of a photocatalytic performance using an ANN model instead of the commonly employed removal efficiency (%) (Antonopoulou et al., 2012).

4.2 Optimization of the photocatalytic system

The implementation of an EA optimization approach to the ANN model resulted in the identification of the maximum k_{app} value corresponding to the optimal degradation of BPA and to the synthesis conditions of the catalytic system Ag/ZnO.
The results of the optimization of the objective function obtained by use of Equation 4 show (Table 3) that (i) a low silver content of the catalytic system Ag/ZnO and (ii) pH values near the point of zero charge of ZnO (pH_{PZC} = 8.2), allowed obtaining the maximum apparent rate constant of BPA degradation. This result can be explained, at such pH, by both the minimal repulsion forces between the non-ionized BPA molecules and

Ag/ZnO photocatalyst surface and the increased generation of hydroxyl radicals (•OH). The optimal AgNPs nominal amount, pH and time of the synthesis of the new catalytic system obtained from the second optimization step are shown in Table 3. The optimized results suggest an alkaline pH for the attachment of AgNPs on the ZnO surface by both methods. Furthermore, the ANN model coupled to EA confirms the significance of the operating conditions, such as the pH, on the synthesis of the catalytic system Ag/ZnO, given the source of silver used in this work (stabilized silver nanoparticles) in contrast with the ones reported in the literature (Peng et al., 2007)..

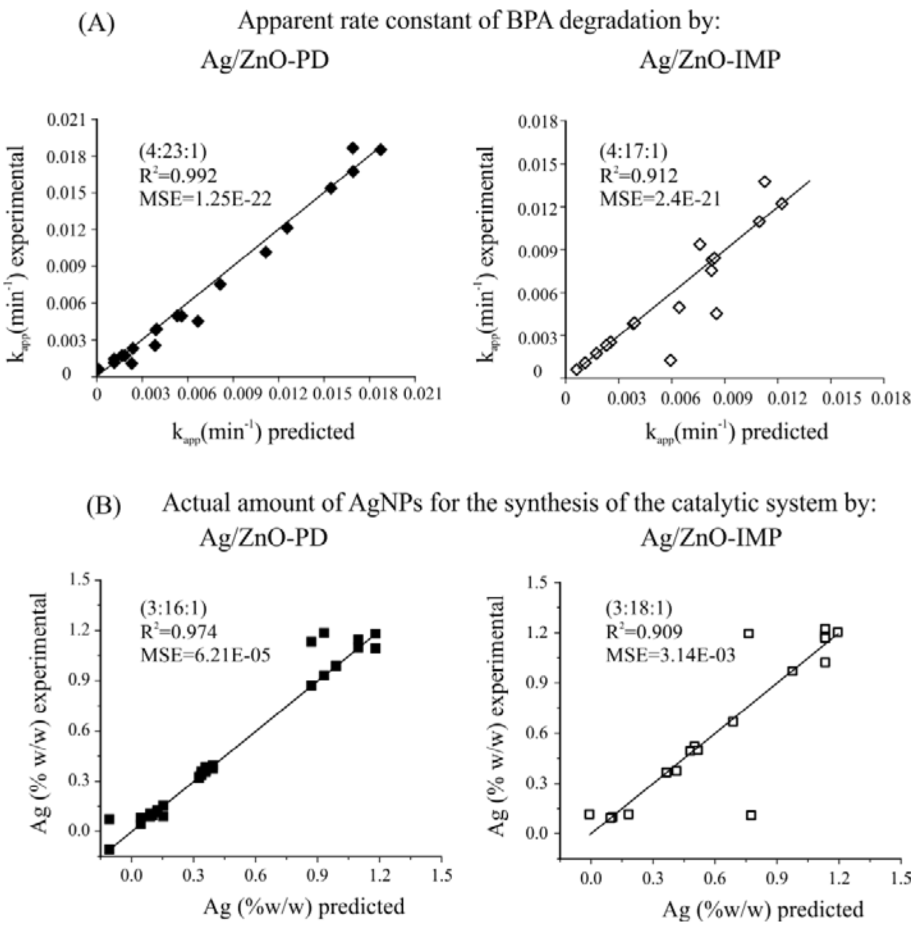

Figure 3: Plots of experimental data versus the predictions of the ANN models A (top) and B (bottom), using Ag/ZnO-PD and Ag/ZnO-IMP catalysts. The corresponding optimal network structures are also provided (In:Hid:Out).

Table 3: Optimal conditions for the photodegradation of bisphenol-A using Ag/ZnO catalytic systems

Variables	Ag/ZnO-PD	Ag/ZnO-IMP
Objective function-Model B		
pH	10.5	8.1
Actual AgNPs amount (% w/w)	0.31	0.44
BPA concentration (mg/L)	19.14	19.93
Wavelength (nm)	315.4	266.6
ANN predicted K_{app} (min^{-1})	0.0202	0.0153
Objective function-Model A		
Nominal AgNPs amount (%w/w)	0.35	0.53
Initial pH	9.1	9.7
Time (min)	41.97	145.08
ANN predicted actual AgNPs amount (%w/w)	0.3062	0.4387

5. Conclusion

The scope of this study was to evaluate the photocatalytic efficiency of Ag/ZnO for the degradation of BPA in aqueous solutions, through a modeling and optimization approach, based on the rate of BPA degradation dynamics.
This approach was considered preferable than a simple optimal final BPA conversion that would be subject to the necessity of selection of an optimal experimental time. Moreover, the degradation rate and conversion are, both, important parameters to reactor design. However, from a practical point of view, kinetics must be considered first since it is more important to obtain a reasonable conversion (as high as possible) in the shorter time possible. Thus, the optimization of degradation rate was considered over conversion.
Therefore, the novelties of this work were the modeling of the complete photocatalytic system using a single response variable and without including time in the model input.
An artificial neural network two-step modeling method was used for (i) the synthesis of Ag/ZnO and (ii) its subsequent use for BPA degradation. The resulting models showed an acceptable accuracy and high predictive capacity.
Finally, the coupling of those models to an evolutionary algorithm resulted in a successful correlation between the catalyst structure and its photocatalytic performance in terms of its metal content (AgNPs) as the convergence point.
This optimization study aims at the possibility to eventually manufacture engineered photocatalysts that lead to a desired performance for the degradation of endocrine disruptor compounds.

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