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Photocatalytic degradation of pollutants from Elcogas IGCC power station effluents

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Abstract

The aim of this work is to improve the quality of water effluents coming from Elcogas IGCC power station (Puertollano, Spain) with the purpose of fulfilling future more demanding normative, using heterogeneous photocatalytic oxidation processes (UV/H_2O_2/TiO_2 or ZnO). The efficiency of photocatalytic degradation for the different catalysts (TiO_2 and ZnO) was determined from the analysis of the following parameters: cyanides, formates and ammonia content.

In a first stage, the influence of two parameters (initial concentration of H_2O_2 and amount of catalyst) on the degradation kinetics of cyanides and formates was studied based on a factorial experimental design. pH was always kept in a value >9.5 to avoid gaseous HCN formation. The degradation of cyanides and formates was found to follow pseudo-first order kinetics. Experimental kinetic constants were fitted using neural networks (NNs). The mathematical model reproduces experimental data within 90% of confidence and allows the simulation of the process for any value of parameters in the experimental range studied. Moreover, a measure of the saliency of the input variables was made based upon the connection weights of the neural networks, allowing the analysis of the relative relevance of each variable with respect to the others. Results showed that the photocatalytic process was effective, being the degradation rate of cyanides about five times higher when compared to removal of formates.

Finally, the effect of lowering pH on the degradation of formates was evaluated after complete cyanides destruction was reached (10 min of reaction). Under the optimum conditions (pH 5.2, [H_2O_2] = 40 g/l; [TiO_2] = 2 g/l), 100% of cyanides and 92% of initial NH_3 concentration are degraded after 10 min, whereas 35 min are needed to degrade 98% of formates.
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1. Introduction

Heterogeneous photocatalysis is an effective treatment method for removal of toxic pollutants from industrial wastewaters [1,2]. In recent years, the success of laboratory work has led to interest in applying this technology to environmental remediation and treatment of process waste streams [3]. Progress has been significant and some companies now provide turnkey systems for treating contaminated water. However, although more than 1000 compounds have been individually studied, industrial waste waters usually contain more than one important pollutant, so that a combined study is necessary for each real case.

In this work, the quality of aqueous effluents coming from Elcogas IGCC power station (Puertollano, Spain) will be improved with the purpose of fulfilling future more demanding normative. To that end, the most important pollutants present in the water (cyanides, formates and ammonium) are analyzed simultaneously. The nature of the photocatalyst determines the rate and efficiency of the process [3]. Those used during this investigation have already been tested in recent literature for similar applications: photocatalytic oxidation of cyanides with TiO_2 based catalysts [4,5], catalytic abatement of water pollutants including ammonia and cyanides [6] and photocatalytic degradation of iron-cyanocomplexes [7].

In this study, the degradation kinetics of the pollutants will be studied combining ultraviolet radiation and hydrogen peroxide in the presence of solid catalysts (TiO_2 and ZnO). A factorial experimental design will be performed for each catalyst. Finally,

results from experimental tests will be fitted using NNs, allowing the values of kinetic rate constants to be estimated within the studied range as a function of process parameters (initial concentration of H_2O_2 and amount of catalyst). In this way, optimum conditions for industrial operation can be obtained. Also, the individual effect of each variable involved can be determined.

Finally, the effect of lowering pH on the degradation of formates will be evaluated after complete cyanides destruction is reached.

2. Experimental

2.1. Catalysts characterization

The anatase form of titanium dioxide has the desirable properties of being chemically stable, readily available, and active as a catalyst for oxidation processes. The 3.2 eV band gap matches the output of a wide variety of accessible lamps. Rutile has a smaller band gap (3.0 eV), but few reports observe photocatalytic activity of this from [3]. Crystallinity and phases present in our catalysts were determined by X-ray diffraction (XRD), using Cu Kα radiation (Ni-filtered), by means of a Philips PW-1700 powder diffractometer and comparing it with a pattern.

Total surface values and pore size data were determined from nitrogen adsorption and desorption data acquired on a Micromeritics Asap 2010 apparatus using a BET method with an experimental error lower than 2%. The samples were pretreated overnight at 350 °C under a vacuum of 6.7×10^{-4} Pa.

2.2. Materials

About 30% hydrogen peroxide (H_2O_2) was purchased from Merck and used as received. Catalysts employed were technical grade TiO_2 P-25 (anatase/rutile = 3.6/1) from Degussa and ZnO (99.5% purity) from Fluka.

2.3. Photochemical reactions

All experiments were carried out in a stirred 400 ml photoreactor with an external jacket connected to a thermostatic bath and able to maintain the temperature constant ± 0.5 °C. A Heraeus TQ150 UV Hg immersed lamp with a nominal output of 150 W and emitting at λ = 190–280 nm irradiated the solutions (Fig. 1). When the effect of pH was studied, it was adjusted (between 2 and 6.5) by using H_3PO_4/NaOH buffer solutions.

Waste waters coming from the gasification unit upstream its treatment at site, contained up to 10 ppm of cyanides, 1700 ppm of formates and 150 ppm of ammonium and were treated using a coagulation–floculation method prior to photocatalytic reaction. Nowadays, these waters are being treated with ozone.

2.4. Analysis of pollutants

Formates were analyzed by high performance ion chromatography using a Methrom chromatograph fitted with an ASUPP5 250 column and an ionic conductivity detector at 10–12 MPa of pressure. The 0.7 ml/min of a 50/50 NaHCO₃ 1 mM/Na₂CO₃
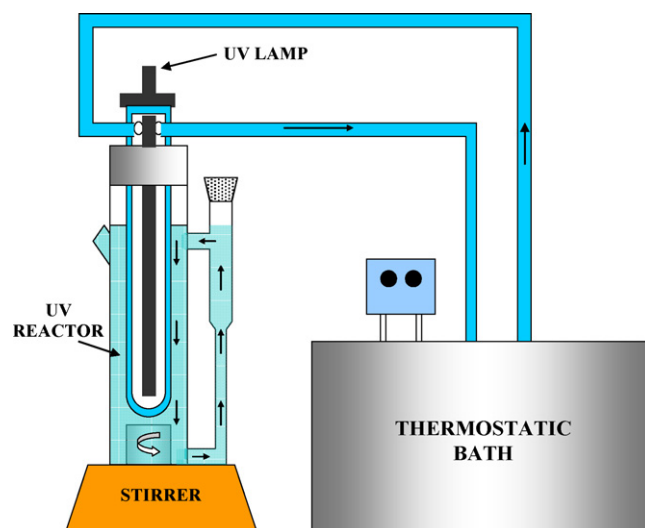

Fig. 1. Experimental set-up.

3.2 mM solution was used a moving phase. The 0.33 ml/min of deionized water and 0.5 ml/min of sulfuric acid (50 mM) were used for the suppression module.

Total cyanide and ammonia concentrations were measured using a continuous flow analyser (FLOWSYS) combining higher performances and low running costs developed by SYSTEA. This method determines the sum of organically bound cyanides, free cyanides ions, complex compounds and simple bound metal cyanides, except cyanides from cobalt complexes. Complex bound cyanide is decomposed at pH 3.8 in a continuously flowing stream by the effect of UV radiation (350 nm, quartz coil). UV light below 290 nm is not active to prevent at pH 3.8 the conversion of thiocyanate into cyanide. The resulting hydrogen cyanide is separated by on-line distillation in acid condition (pH 3.8) at 125 °C. Cyanide are transformed into cyanogens chloride (CNCl) with Chloramin-T. CNCl reacts with 1,3-dimethylbarbituric acid and pyridin-4 carbonic acid (isonicotinic acid) in buffered condition and gives a red colored complex measured at 600 nm.

Ammonia was analyzed using the Berthelot reaction, in which a blue–green coloured complex is formed. A complexing reagent is used to virtually eliminate the precipitation of calcium and magnesium hydroxides. Sodium nitroprussiate is used to enhance the sensitivity of this method.

2.5. Experimental design

For the first set of experiments, a central composite experimental design was applied to investigate the effect of two variables: initial concentrations of H_2O_2 and catalyst on two response functions (cyanides and formates degradation rates, k_{CN^-} and k_{HCOO^-}). It consists of three series of experiments for each catalyst (TiO₂ or ZnO) [8]:

(i) a factorial design 2^k (all possible combinations of codified values +1 and −1), which in the case of $k = 2$ variables consists of four experiments;

(ii) axial of star points (codified values $\alpha = 2^{k/4} = \pm 1.414$) consisting of $2k = 4$ experiments;

(iii) central, replicates of the central point (three experiments).

The complete experimental design (including variables ranges and responses) is shown in Table 1. Since, its possible industrial use would require temperatures close to ambient, this parameter was kept in 20 °C. The initial rate of degradation of formates and cyanides was found to obey pseudo-first order kinetics. The values of the kinetic constants (k_{CN^-} and k_{HCOO^-}) obtained from the first 10 min of reaction (response functions) are also resumed in Table 1.

2.6. Neural network strategy

Neural networks are formed by input data vectors, neurons and output functions. Input data to the neuron are transformed by means of a base function and leave by an activation function. Each connection between input and output data and neurons is made by weight factors W_{ij}, which determine the effect of the input variable i on the neuron j. In this work, a Linear Basis Function (linear combination between inputs, X_j, and weight factors, W_{ij}) was used:

$$U_i = \sum_{j=1}^{n} W_{ij} X_j \tag{1}$$

Each neural network applied in this work is solved with two neurones and uses a simple exponential activation function [9]:

$$f(U_i) = \frac{1}{1 + e^{-U_i}} \tag{2}$$

Input variables in this study are initial concentration of hydrogen peroxide and catalyst; output data are cyanides and formates degradation constant.

The strategy is based on a back propagation calculation. Parameters are found using the solver tool in an in-house Excel spreadsheet and using the Marquardt non-linear fitting algorithm [10]. Further details can be found in literature [11].

Neural networks in this work are used only as an interpolation function. Since, data is scarce and difficult to obtain, all the data have been used for validation and testing. The weight factors were obtained by non-linear fitting and can be considered for the other conditions without further training if they are within the experimental range of the studied variables.

Table 1
Central composite experimental design for the photocatalytic degradation of pollutants from Elcogas IGCC power station effluents

Experimental design			Responses			
			TiO₂		ZnO	
Experiment	[H₂O₂] (g/l)	[Catalyst] (g/l)	k_{CN} (min⁻¹)	k_{HCOO} (min⁻¹)	k_{CN} (min⁻¹)	k_{HCOO} (min⁻¹)
1	8.68	1.04	0.39	0.063		
2	2.32	1.04	0.2844	0.038		
3	8.68	0.26	0.3418	0.028		
4	2.32	0.26	0.2932	0.039		
5	10.00	0.65	0.346	0.069		
6	1.00	0.65	0.078	0.006		
7	5.50	1.20	0.355	0.049		
8	5.50	0.10	0.281	0.051		
9	5.50	0.65	0.386	0.054		
10	5.50	0.65	0.390	0.063		
11	5.50	0.65	0.375	0.058		
12	8.68	1.04			0.276	0.059
13	2.32	1.04			0.212	0.025
14	8.68	0.26			0.253	0.072
15	2.32	0.26			0.1985	0.057
16	10.00	0.65			0.2687	0.052
17	1.00	0.65			0.094	0.013
18	5.50	1.20			0.219	0.045
19	5.50	0.10			0.226	0.073
20	5.50	0.65			0.280	0.059
21	5.50	0.65			0.252	0.053
22	5.50	0.65			0.261	0.055
Levels						
(+α)	10	1.20				
(−α)	1	0.1				
(+1)	8.68	1.04				
(−1)	2.32	0.26				
(O)	5.5	0.65				

Table 2
Equation and parameters of the NNs fittings

Neurons and weight factors	Parameters	TiO$_2$		ZnO	
		Values of neurons and factors to obtain the cyanides degradation constant, k_{CN} (min^{-1})	Values of neurons and factors to obtain the formates degradation constant, k_{HCOO} (min^{-1})	Values of neurons and factors to obtain the cyanides degradation constant, k_{CN} (min^{-1})	Values of neurons and factors to obtain the formates degradation constant, k_{HCOO} (min^{-1})
$k[\text{min}^{-1}] = N_1*(1/(1 + 1/\exp([H_2O_2]*W_{11} + [\text{catalyst}]*W_{12}))) + N_2*(1/(1 + 1/\exp([H_2O_2]*W_{21} + [\text{catalyst}]*W_{22})))$					
N_1	Neuron	−0.2607	−0.0524	−0.2150	0.0048
W_{11}	[H$_2$O$_2$]	−0.5709	1.4965	−0.9384	1.3186
W_{12}	[Catalyst]	−6.8203	−5.4625	−7.2635	−5.4034
N_2	Neuron	0.3923	0.0603	0.2831	0.0584
W_{21}	[H$_2$O$_2$]	21.5022	24.0511	14.6215	23.6736
W_{22}	[Catalyst]	−2.5426	−3.5098	−1.2220	−4.3910

*Parameters values [H$_2$O$_2$] and [catalyst] must be previously normalized to the (0, 1) interval.

Finally, a measure of the saliency of the input variables was made based upon the connection weights of the neural networks [12]. This study allows analysis of the relevance of each variable with respect to the others (expressed as a percentage). Such evaluation allows the researcher to retain the important variables in the model and discard less important ones.

3. Results and discussion

3.1. Neural network fitting for UV/H$_2$O$_2$/TiO$_2$ and UV/H$_2$O$_2$/ZnO systems

Experimental results and NNs fittings, shown in Fig. 2, are in good agreement, with an average error lower than 5% for the cyanides degradation rate constant (k_{CN^-}) and 9% for the formates degradation rate constant (k_{HCOO^-}). Scattering may be due to small changes in pH during reaction (from 8.5 to 9.7), what may cause small variations in the values of the kinetic constants.

The equation and parameters for the fitting of both kinetic constants using NNs are shown in Table 2. N_1 and N_2 are general factors related to the first and the second neuron, respectively. W_{11} to W_{12} are the contribution parameters to the first neuron and represent the influence of each of the variables in the process (initial concentration of H$_2$O$_2$ and catalyst); W_{21} to W_{22} are the contributions to the second neuron and are related to the same variables.

The results of a saliency analysis on the input variables for each neural network (%) are shown in Table 3. From these results it is possible to deduce the effect of each parameter on

Table 3
Saliency analysis of the input variables for each neural network (%)

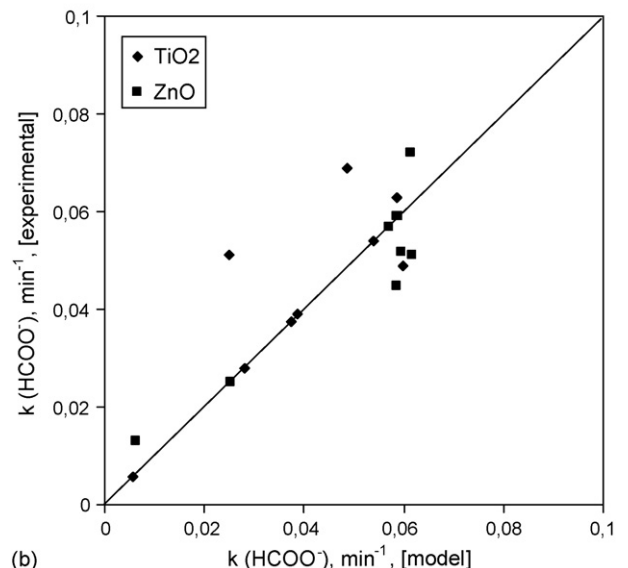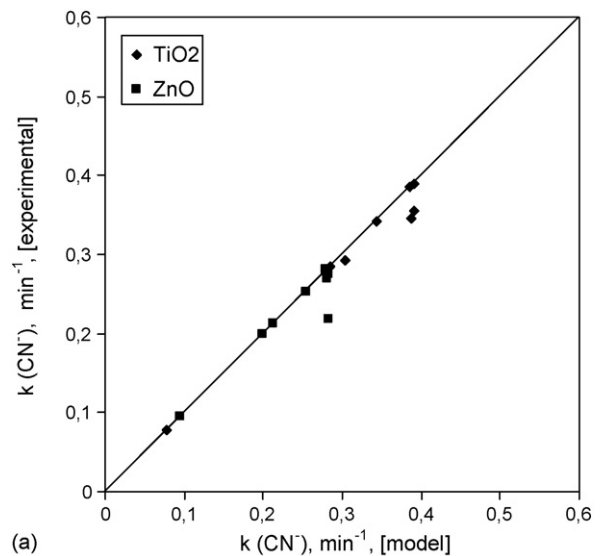| Neural network output	TiO$_2$		ZnO	
	[H$_2$O$_2$]	[Catalyst]	[H$_2$O$_2$]	[Catalyst]
Cyanides degradation constant, k_{CN} (min^{-1})	48.58	51.42	51.86	48.14
Formates degradation constant, k_{HCOO} (min^{-1})	54.39	45.61	51.98	48.02

Fig. 2. Neural networks fitting of kinetic degradation constants. (a) Cyanides; (b) formates.

the variable studied. In this study, it is confirmed that relating the degradation of both pollutants, the initial concentrations of hydrogen peroxide and catalyst have approximately the same importance.

3.2. Effect of initial concentrations of H_2O_2 and catalyst on degradation rate constants

Equations shown in Table 2 allow a simulation analysis of the effect of the studied variables on the value of the degradation constants. Thus, the influence of H_2O_2 and catalyst concentration on the degradation kinetic constants of cyanides and formates are shown in Figs. 3 and 4, respectively.

From these figures we can deduce:

(i) Under the best conditions into the experimental range, the degradation rate of cyanides is about five to six times higher than that of formates for both catalysts (TiO$_2$ and
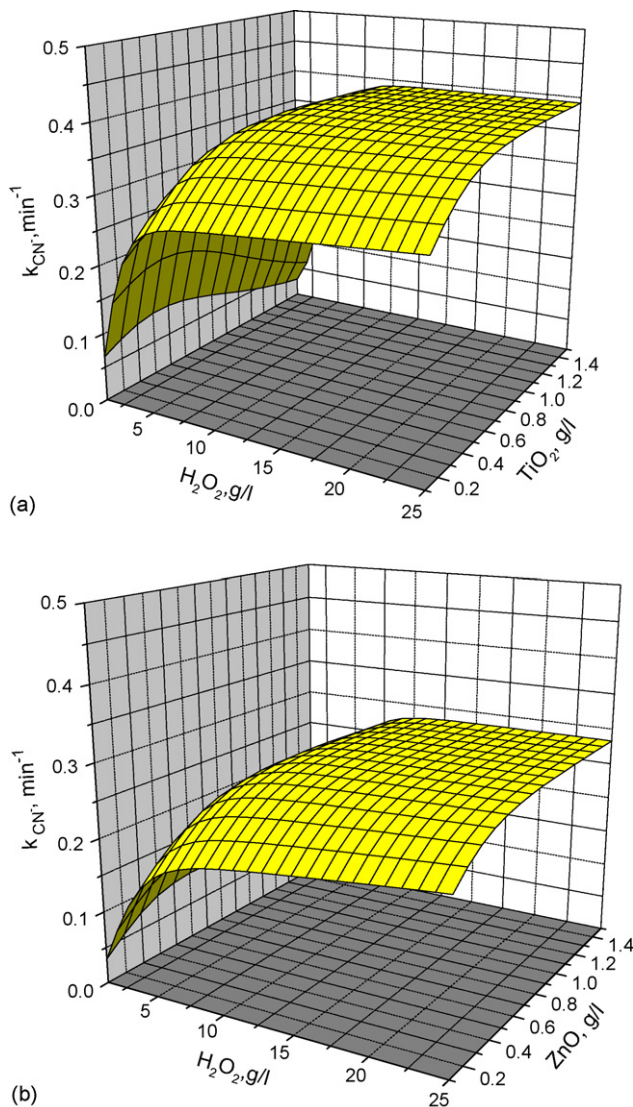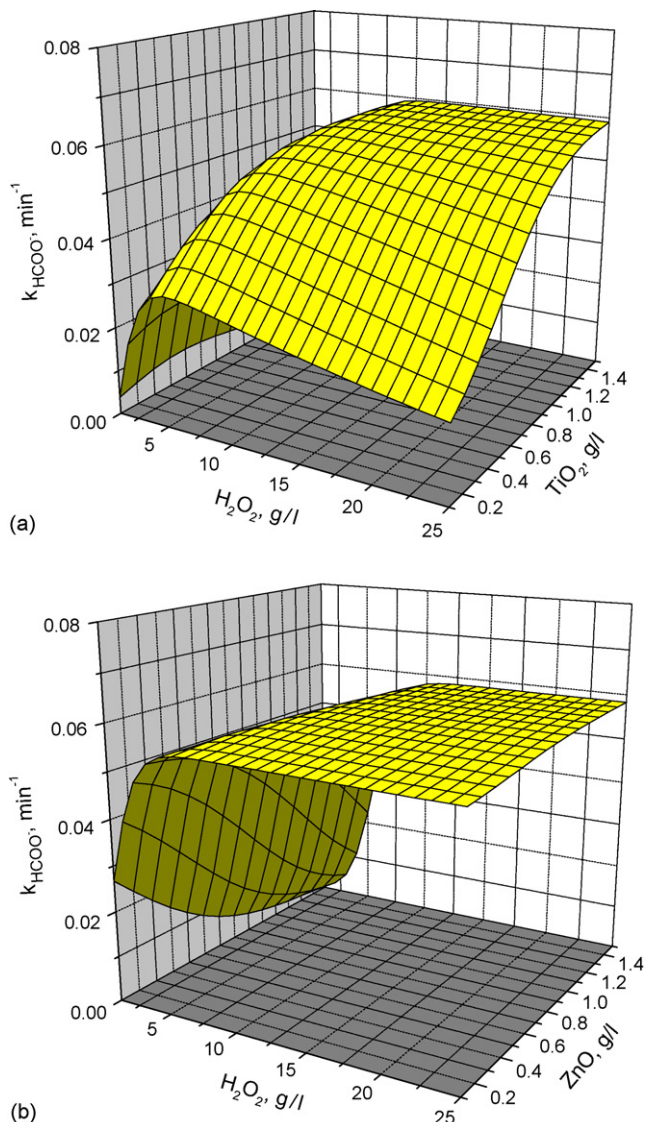
(a)

(b)

Fig. 4. NNs simulations: effect of initial concentration of hydrogen peroxide and catalyst on formates degradation constant (pH 9.5). (a) TiO$_2$-P25; (b) ZnO.

ZnO). Cyanides can be degraded both via a molecular route (direct reaction with hydrogen peroxide) and reaction with $^{\bullet}OH$ radicals, whereas formates are degraded by the radical route alone. The competition for adsorption sites between cyanide and formate ions is significantly in favour of cyanide ions.

(ii) The addition of TiO$_2$ in the presence of hydrogen peroxide slightly improves the degradation rate of cyanides. The maximum kinetic rate constant is $0.4\,min^{-1}$.

(iii) The addition of TiO$_2$ in the presence of hydrogen peroxide improves the degradation rate of formates. The zero point charge for TiO$_2$-P25 is located at pH between 5.6 and 6.4 [13]. Under the experimental conditions (pH > 9.5), titanium dioxide is negatively charged by adsorbed OH$^-$ ions, favoring the formation of strongly oxidant $^{\bullet}OH$ radicals [14] and to some extent helping in the degradation process.

(iv) The addition of ZnO in the presence of H_2O_2 does not significantly affect the degradation of cyanides which is

(a)

(b)

Fig. 3. NNs simulations: effect of initial concentration of hydrogen peroxide and catalyst on cyanides degradation constant (pH 9.5). (a) TiO$_2$-P25; (b) ZnO.

mainly occurring via molecular route (maximum rate constant = 0.3 min^{-1}).

(v) However, an increase in ZnO concentration above 0.1 g/l does not improve the degradation process of formates. Moreover, when a low concentration of hydrogen peroxide is used, the effect of increasing ZnO concentration is even negative. This may be due to the strong pH dependence of ZnO which is consistent with its bare surface [15] (BET surface area = 3.97 m^2/g; micropore volume = 0.017 cm^3/g) compared with titanium dioxide (BET surface area = 50.56 m^2/g; micropore volume = 0.274 cm^3/g) as explained below. The zero point charge for ZnO is 9.0 above which ZnO surface is negatively charged. However, under experimental conditions (pH 8.5–9.7), the mere electrostatic argument is unable to account for the relative photocatalytic behaviour as a function of pH. Other effects such us photocorrosion through self-oxidation, dissolution in a strongly alkaline media or formation of photocatalytically inert Zn(OH)$_2$ surface layers upon UV irradiation can come into play inhibiting the catalyst activity [15]. Moreover, an increase in catalyst concentration could give place to an increased opacity of the suspension producing a decrease in light penetration into the suspension with the consequent reduction in the formation of $^\bullet$OH radicals.

(vi) Optimal removal of both specie are obtained when high concentrations of hydrogen peroxide (20–25 g/l) and TiO$_2$ (>1 g/l) are used.

From these results, it is possible to select the UV/H$_2$O$_2$/TiO$_2$ system as more appropriate for the degradation of pollutants from Elcogas IGCC power station effluents. However, under these conditions (initial pH 9.5), the degradation rate of formates is still very low.

3.3. Effect of pH for the selected UV/H$_2$O$_2$/TiO$_2$ system

Thus, in order to complete the study, and trying to accelerate the degradation of formates, a new factorial design was performed changing pH conditions from 2 to 6.5, close to the neutrality point of TiO$_2$. pH was lowered after 10 min of reaction to ensure that 100% of cyanides had been previously degraded. As already mentioned, the zero point charge for TiO$_2$-P25 is at pH between 5.6 and 6.4. Hence, at more acidic pH values, the TiO$_2$ surface is positively charged and favours the adsorption of formates which are negatively charged. The complete experimental design and variables range are shown in Table 4.

Results from NNs fitting have an average error lower than 10% for the formates degradation constant (k_{HCOO^-}). Equation and parameters for the fitting of the formates degradation constant is shown in Table 5.

NNs simulation (Fig. 5) shows that optimum conditions are found for pH 5.2 and [TiO$_2$] = 2.0 g/l. The maximum degradation rate constant for formates under these conditions is 0.1 min^{-1} which is about 70% higher than the value obtained without pH modification ($k = 0.06$ min^{-1}). Very low pHs are disadvanta-
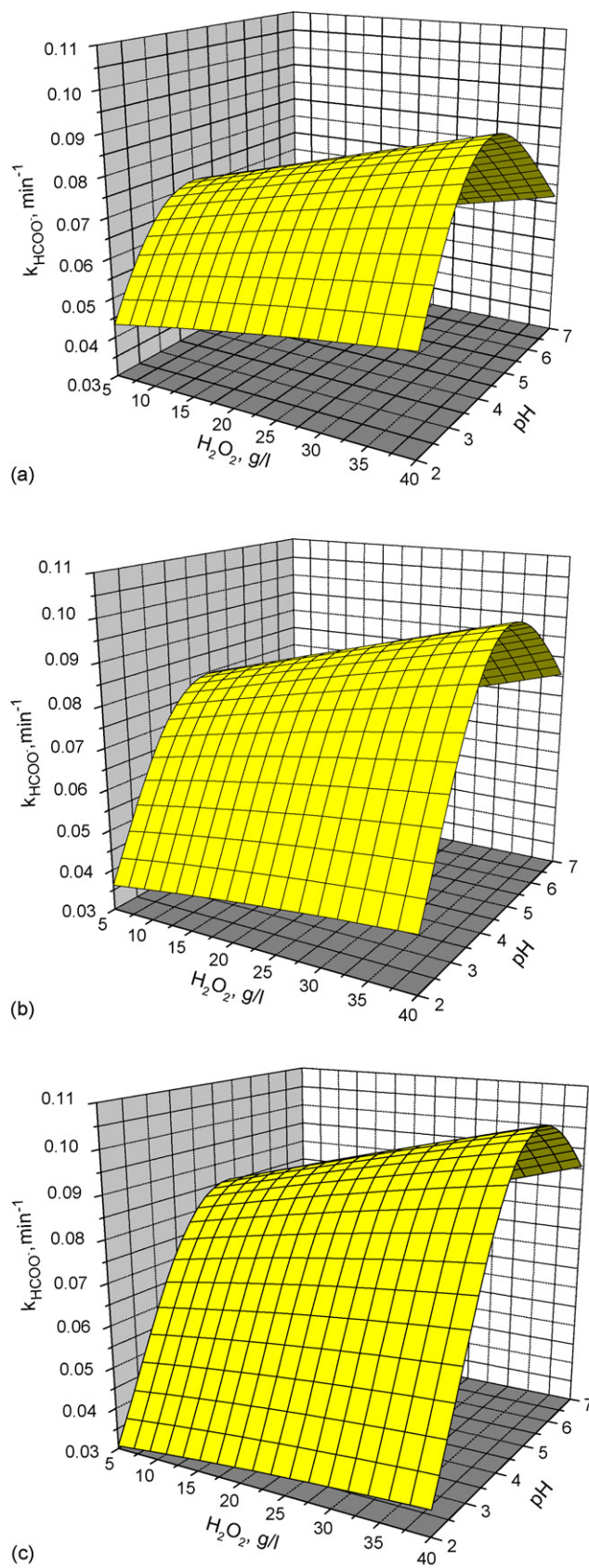

Fig. 5. NNs simulation. Effect of pH and initial concentration of hydrogen peroxide for the UV/H$_2$O$_2$/TiO$_2$ system. (a) [TiO$_2$] = 1.5 g/l; (b) [TiO$_2$] = 1.8 g/l; (c) [TiO$_2$] = 2.0 g/l.

Table 4
Central composite experimental design for the study of pH in the photocatalytic degradation of formates from Elcogas IGCC effluents for the UV/H₂O₂/TiO₂ system

Experimental design				Response
Experiment	$[H_2O_2]$ (g/l)	pH	TiO_2 (g/l)	k_{HCOO} (min^{-1})
1	32.91	5.58	1.695	0.0882
2	12.09	5.58	1.695	0.0810
3	32.91	2.91	1.695	0.0245
4	12.09	2.91	1.695	0.0200
5	32.91	5.58	0.804	0.0839
6	12.09	5.58	0.804	0.0550
7	32.91	2.91	0.804	0.0364
8	12.09	2.912	0.804	0.0358
9	40	4.25	1.250	0.0767
10	5	4.25	1.250	0.0594
11	22.5	6.5	1.250	0.0643
12	22.5	2	1.250	0.0210
13	22.5	4.25	2.000	0.0549
14	22.5	4.25	0.500	0.0552
15	22.5	6.325	1.250	0.0591
16	22.5	4.977	1.250	0.0788
17	22.5	4.54	1.250	0.0866
Levels				
$(+\alpha)$	40	6.5	2	
$(-\alpha)$	5	2	0.5	
$(+1)$	32.91	5.59	1.70	
(-1)	12.09	2.91	0.80	
(O)	22.5	4.25	1.25	

geous, since, TiO₂ particles agglomeration reduces the formates adsorption and photon absorption [16].

Saliency analysis shows that pH is the main variable influencing the degradation rate of formates (54.2%), followed by TiO₂ concentration (38.5%) and H₂O₂ concentration (7.3%).

Finally, Fig. 6 shows the pollutants evolution for the best conditions found in this work (pH 5.2, $[H_2O_2] = 40$ g/l; $[TiO_2] = 2.0$ g/l). It can be seen that after 10 min, 100% of cyanides and 92% of ammonia are destructed, whereas 35 min are needed to degrade 98% of formates initially present in water.

Table 5
Equation and parameters of the NNs fitting for the study of pH in the photocatalytic degradation of formates from Elcogas IGCC effluents for the UV/H₂O₂/TiO₂ system

Neurons and weight factors	Parameters	Values of neurons and factors to obtain the formates degradation constant, k_{HCOO} (min^{-1})
$k[min^{-1}] = N_1*(1/(1 + 1/exp([H_2O_2]*W_{11} + pH*W_{12} + W_{13}*[TiO_2])))$		
$+ N_2*(1/(1 + 1/exp([H_2O_2]*W_{21} + pH*W_{22} + W_{23}*[TiO_2])))$		
N_1	Neuron	−0.1369
W_{11}	$[H_2O_2]$	−0.6657
W_{12}	pH	2.2705
W_{13}	$[TiO_2]$	−2.3403
N_2	Neuron	0.16369
W_{21}	$[H_2O_2]$	−0.1527
W_{22}	pH	4.9016
W_{23}	$[TiO_2]$	−2.4412

*Parameters values $[H_2O_2]$, pH and $[TiO_2]$ must be previously normalized to the (0, 1) interval.
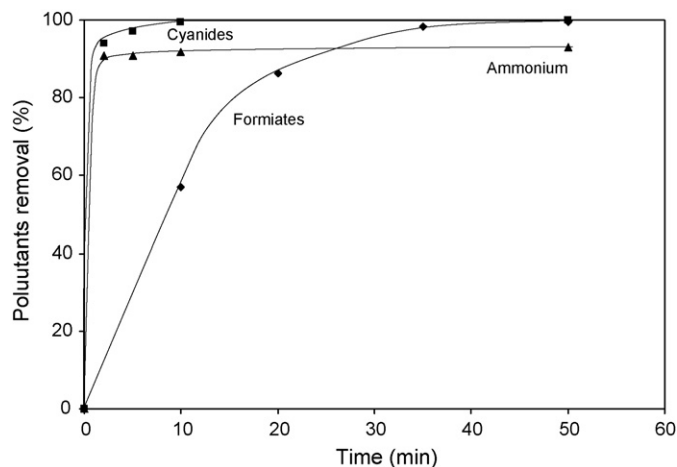

Fig. 6. Degradation of pollutants for optimum conditions using a UV/H₂O₂/TiO₂-P25system (conditions: pH 5.2; $[H_2O_2] = 40$ g/l; $[TiO_2] = 2.0$ g/l).

4. Conclusions

- Simulation from NNs equations proves that H₂O₂ and catalyst concentrations are the main parameters affecting the photodegradation of cyanides, whereas pH is the main variable involved when formates are being degraded.
- The degradation rate of cyanides using heterogeneous photocatalysis (UV/H₂O₂/TiO₂-P25) is about five to six times faster than the removal rate of formates. Optimum conditions without pH modification are obtained when high concentrations of hydrogen peroxide (20–25 g/l) and TiO₂ (>1 g/l) are used.
- The optimum conditions after pH modification ($[H_2O_2] = 40$ g/l; $[TiO_2] = 2.0$ g/l, pH 5.2) produces an increase in the kinetic rate constant of formates (from 0.06 to 0.1 min^{-1}). Under these conditions, it is possible to degrade 100% of cyanides and 92% of ammonia in 10 min, and 98% of formates in 35 min.
- The addition of ZnO in the presence of H₂O₂ does not significantly affect the degradation of cyanides which is mainly occurring via molecular route (maximum rate constant = 0.3 min^{-1}). Relating the degradation of formates, when a low concentration of hydrogen peroxide is used, the effect of increasing ZnO concentration is even negative.
- The use of a low cost catalyst and its activation with UV light can offer an economical and practical alternative for the destruction of environmental pollutants present in thermoelectric power stations effluents.

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