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Hybrid Model of a Wastewater-Treatment Electrolytic Process

Ciprian-George Piuleac[1], *Cristina Sáez*[2,*], *Pablo Cañizares*[2], *Silvia Curteanu*[1], *Manuel Andrés Rodrigo*[2]

[1] Faculty of Chemical Engineering and Environmental Protection, "Gh. Asachi" Technical University of Iasi, Bd. D. Mangeron, No. 71A, 700050 Iasi, Romania
[2] Department of Chemical Engineering, Universidad de Castilla La Mancha, Campus Universitario s/n 13071 Ciudad Real, Spain
[*]E-mail: Cristina.saez@uclm.es

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This work is focussed on the development of models which can be implemented in efficient control devices to properly schedule batch electrolysis processes for wastewater treatment. The main goal has been to develop a hybrid approach based on a phenomenological mathematical model and a neural network methodology, in order to improve the quality of the model designed for electrolysis process of wastewaters. A well-known phenomenological model for the electrolyses of wastewaters and different neural network architectures were used, along with homogenous and heterogenous transfer functions. The models were validated with the results of a series of experiments consisting of the electrochemical oxidation of phenol wastes in different process conditions. The best results were obtained designing a feed-forward neural network with tangent hyperbolic axon as homogeneous transfer function (relative error of 8 %).

Keywords: hybrid model, neural networks, electrolyses, wastewater

1. INTRODUCTION

Recently, electrochemical wastewater treatment processes have become a real possible option in the treatment of industrial wastes flows, in particular in the cases where the characteristics of pollutants imposed a better alternative choice against the employment of biological or incineration technologies. There are many works published concerning the use of electrolyses in the treatment of synthetic wastewaters and actual wastewaters. Within these technologies, the use of diamond anodes has given an important advantage due to the great removals of COD (no refractory compounds are formed) and to the great energy efficiencies of these processes [1]. This fact has promoted that during

the last years many studies were focused on the scale-up of these treatment processes, in order to evaluate its possible use in industrial scale.

The design techniques of a phenomenological model based on a chemical process are requiring for many difficulties to overpass, especially when a limited knowledge is available. One alternative choice to overcome these problems could be based on neural networks tools. The advantages like the possibility to apply it on complex non-linear processes, the ease in manipulation and saving money and time, seem to create the opportunity to substitute experiments with predictions. On the other side, the disadvantages could be upon the necessity in obtaining a perfect neural network model based on experimental or operational history data, this approaching being not easy to put in practice. Generally, the approach based on neural networks does not lead to a clarification on the mechanism on modeled process. For this reason, the both approaches, mechanistic and neural, could be complementary to one another. On one side, the phenomenological model relieves the physical and chemical laws that govern the system and, on the other side, the neural model, with its empirical characteristics, could develop and lead to more precisely solutions.

In the last years, several phenomenological models [2-5] have been proposed trying to explain the mechanisms concerned in the electrochemical processes involved in the treatment of wastewaters, but they cannot be easily to develop and use for predicting the behavior of the systems. In this way, artificial neural networks appear as a promising alternative tool for classical process modeling. The neural networks behave as 'black boxes' and they can be simply used to estimate different parameters as a function of time or current to attain fixed final conditions of the treated effluent [6].

Once the viability of the electrochemical process has been confirmed for a particular wastewater, the development of efficient operation procedures becomes an important topic and makes possible the use of the technology in industrial applications [6-8]. It is worth to note that electrolytic wastewater treatment processes should be usually operated in a batch mode, because its objective is the treatment of particular wastes which cannot be treated with other cheaper technologies and usually the amount of these wastes is small and they come from very different processes. The variety of characteristics in the wastes incoming in a treatment plant of a typical waste-management company requires a deep study to establish the suitable operation conditions and thus, the proper schedule of batches in a scheduled manufacturing control system. As it is known, in every batch it is required to decrease the organic load down to the discharge limit fixed by the authority and the electrolyzer works in an uninterrupted way starting again a cycle when a batch is completed. In these systems, the electrolysis time (or more properly, the current charge required) is the more important operation parameter, because it allows optimizing the management of different wastes in a waste treatment plant by selecting the proper operation schedule.

The final product of the neural network modeling is represented by a trained network that provides no equations or coefficients defining a relationship (as in regression) beyond its own internal mathematics. In other words, neural network needs good quality data (large amount of data which cover the whole range of the process variable) for its training, which is normally difficult to obtain in practice. Any applications prove that if properly trained and validated, the neural network models can be used to accurately predict the process behavior, hence, leading to improve process optimization and control performance [9].

The main goal of the present paper is to emphasize the option by using a hybrid model based on a combination between a phenomenological approach and neural networks with different architectures to model an electrochemical wastewater treatment process. It can be considered as the first step in the development of efficient control devices to properly schedule batch electrolysis processes. To train and validate the networks, a series of experiments have been carried out to study the oxidation of phenolic compounds (phenol, chlorophenols and nitrophenols) in different process conditions. Aside from the experimental part, a modeling methodology was developed to describe the dependencies between the parameters involved into the electrolysis process in order to predict the evolution of COD (Chemical Oxygen Demand) as a function of others parameters of the process.

2. EXPERIMENTAL

2.1. Experimental setups and Analytical procedure

The electrolysis of each organic pollutant was carried out in a single-compartment electrochemical flow cell described elsewhere [10]. Diamond-based material was used as anode and stainless steel (AISI 304) as cathode. Both electrodes were circular (100 mm diameter) with a geometric area of 78 cm^2 each and an electrode gap of 9 mm. The electrolyte was stored in a glass tank (500 ml) and circulated through the electrolytic cell by means of a centrifugal pump. A heat exchanger was used to maintain the temperature at the desired set point. The experimental set-up also contained a cyclone for gas–liquid separation, and a gas absorber to collect the carbon dioxide contained in the gases evolved from the reactor into sodium hydroxide.

Bench scale electrolyses under galvanostatic conditions were carried out. The synthetic wastewaters used in the experiments contained different concentrations of organics (phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 4-nitrophenol and 2,4-dinitrophenol) and 5000 mg dm^{-3} of Na_2SO_4 or Na_3PO_4 as supporting electrolyte. The initial COD used was in the range 45 – 5300 mg L^{-1}. The range of concentration studied was selected taking in to account the typical concentration of this type of pollutant in wastewaters. In some experiments the sulphate anion was replaced by phosphate in order to study the effect of the salts composition. The pH was set at 2 or 12 and it was kept constant by the continuous introduction of sulphuric acid or sodium hydroxide to the electrolyte reservoir. The current density employed was in the range 15–60 mA cm^{-2} and the temperature was ranged from 15 to 60°C. The cell potential was constant during each electrolyses, indicating that appreciable deterioration of the electrode or passivation phenomena did not take place.

Chemical Oxygen Demand (COD) was determined using a HACH DR2000 analyser. The carbon concentration was monitored using a Shimadzu TOC-5050 analyser. Most organic intermediates were identified by chromatography using standards. Thus, carboxylic acids were monitored by HPLC using a Supelcogel H column (mobile phase, 0.15 % phosphoric acid solution; flow rate, 0.15 ml min^{-1}). The UV detector was set at 210 nm. Aromatics were also monitored by HPLC using a Nucleosil C_{18} column (mobile phase, 65 % water / 33 % methanol / 2 % acetic acid; flow rate, 0.50 ml min^{-1}). In this case, the UV detector was set to 280 nm.

2.2 Phenomenological mathematical model

The phenomenological model used in this work was first proposed by the group of Comninellis at the EPFL (Switzerland) and it is based on the modelling of the current efficiency as a function of the chemical oxygen demand of the wastewater contained in the electrochemical cell. From the mathematical point of view, this behavior can be modeled with equations (1) and (2) [2, 11], where the value from which the COD transfer rate limits the overall process rate ($COD_{lim}^{mass transfer}$) is related to the mass transfer coefficient as in the equation (3).

$$\text{If } COD(t) > COD_{\lim}^{mass\ trans\ fer} \text{, then } ICE(t)=1 \quad (1)$$

$$\text{If } COD(t) \le COD_{\lim}^{mass\ transfer} \text{, then } ICE(t) = \frac{COD(t)}{COD_{\lim}^{mass\ transfer}} \quad (2)$$

$$COD_{\lim}^{mass\ transfer} = \frac{j_{appl}}{4 \cdot F \cdot k_m} \quad (3)$$

In the above equations, COD(t) is the COD at time t (mol O_2 m^{-3}), I is the current intensity (A), F is the Faraday constant (96,487Cmol^{-1}), j_{appl} is the applied current density (A m^{-2}) and k_m is the mass transfer coefficient (m s^{-1}). For a typical batch electrochemical system, the following mass balance of the reaction system can be obtained for the reactor volume (Eq. 4).

$$V_R \cdot \frac{dCOD(t)}{dt} = -\frac{I}{4 \cdot F} \cdot ICE(t) \quad (4)$$

According to the models described, the current density is an important operation parameter and it influences directly the $COD_{lim}^{mass\ transfer}$ and, thus, the concentration of pollutant from which the process becomes mass transport controlled. Moreover, the mass transfer coefficient is the lone parameter and it can be easily calculated by a standard ferrocyanide/ferricyanide essay.

According to the literature, this direct oxidation model fits well the experimental data, especially for non-chlorine or nitrogen-substituted aromatics [3,,7]. However, it is known that in the electrochemical oxidation of wastewaters on BDD (Boron Doped Diamond), other oxidants are produced, including persulphates and hydrogen peroxide (depending on the waste composition and the operation conditions) and this produces some deviations in the results of the model [12].

2.3. Neural network strategy

A neural network consists of processing neurons and information flow channels between the neurons, usually called “interconnections”. The knowledge and processing abilities of a layered network are stored on the arrangement of the neurons (number of layers and number of neurons in each

layer), the transfer function associated with each processing element and the value of the weighted links. Each processing neuron calculates the weighted sum of all interconnected signals from the previous layer plus a bias term and then generates an output through its activation transfer function.

The neural network modeling implies the following steps: collecting the data by experiments, making up the training and validation data sets, developing the neural network topology, training and, finally, establishing the performance of the neural network model by comparing the network prediction to unseen (validation) data.

The adjustment of the neural network function to experimental data (learning process or training) is based on a non-linear regression procedure. Training is done by assigning random weights to each neuron, evaluating the output of the network and calculating the error between the output of the network and the known results. If the error is too large, the weights are adjusted and the iteration process is repeated again to evaluate the output of the network. This cycle is repeated till the error is becoming lower or a stop criterion is satisfied.

A network generalized well when the input-output relationships, found by the network, are correctly represented for input/output patterns of validation data, which were never used in training the network (unseen data).

Quality of a model strongly depends of the neural network performance. It is well known that the designing of an efficient neural network is strictly dependent on the amount and appropriateness of the available training data. Our experimental data correspond to this statement from two points of view: a considerable number of experiments were carried out and the chosen conditions cover uniformly the whole domain of interest.

In close correlation with the nature of application and chemical system type, various topologies of neural networks can be applied: multilayered feedforward neural networks (multilayer perceptrons, MLP), generalized feedforward neural networks (GFF), modular neural networks (MNN) or Jordan-Elman neural networks (JEN) [13], stacked neural networks with different or identical neural networks [6, 14].

Hybrid models, based on a simplified phenomenological model and one or several neural networks represent a possibility to improve the neural model performance. Many papers are focused on this methodology where the unknown part of the process can be replaced with a neural network trained with experimental data [15-18]. For instance, Tian et al. (2001) designed a nonlinear hybrid model composed of a simplified phenomenological one (an approximate model that does not consider the diffusional effects of the process) and stacked recurrent neural networks for a batch methyl methacrylate polymerization reactor. Nascimento et al. (1999) applied a similar strategy on nylon-6,6 polycondensation in a twin-screw extruder reactor. A hybrid model, considering the end-use properties of a polyethylene, is developed by Hinchiffe et al (2003).

Curteanu and Leon (2006) present different possibilities in obtaining a hybrid model for a free radical polymerization process. Neural network is a tool to correct the outputs of the simplified kinetic model or to simulate the part of the process which is difficult to model.

The organic nature of compounds in wastewater has a great influence on the efficiency of the electrochemical oxidation. For the case study approached in this paper, the main compounds are

carbon dioxide as product of electrolysis and oxalic acid as intermediate of aromatic compounds. This suggests that breaking the nucleus is faster than oxidation of carboxylic acids.

One of the first steps in the treatment of wastewaters containing aromatic compounds with chlorine or nitro groups is the reduction through the substitution of aromatic groups. Experiments have proven that the main factor in the electrochemical oxidation of aromatic compounds on boron doped diamond anodes is not limited by mass transfer. Given these assumptions, in the designed mathematical modeling for electrochemical oxidation of phenolic compounds, the estimation of COD was considered according to experimental conditions: current intensity applied, solution flow rate and mass transfer coefficient. Also, a modeling methodology based on different types of neural networks (MLP, GFF, MNN or JEN), in combination with a classical mathematical model for an electrolysis process of six phenol compounds is designed in this paper. This technique, including different combinations of transfer functions, has as main purpose obtaining a better generalization capability than the simple models (phenomenological or neural network models).

3. RESULTS AND DISCUSSION

3.1. Processing of experimental data

Figure 1 shows a typical profile of variation of the soluble chemical oxygen demand (COD) with the specific electrical charge passed (Ah L^{-1}) during electrolysis essay with boron doped diamond.

As it can be observed, the complete removal of the soluble organic compounds contained in the waste is obtained. Likewise, the electrolysis leads to the generation of low concentration of intermediates during the first stages of treatment (not shown in the figure) and they are finally oxidized, given to the formation of carbon dioxide as the main final product. The changes in the concentration of COD with the time are linear for very high concentrations of pollutants and exponential for lower concentrations. This has been explained in literature in terms of the process that controls the overall rate of the electrochemical process. Thus, when the concentration is low, the process is mass-transfer controlled and the rate of the process depends directly on the concentration of pollutant. The efficiency increases linearly with the COD during this period. On the contrary, for higher pollutant concentrations, the rate is limited by the Butler-Volmer kinetic and this explains the linear trend. As there is no competing reaction, the efficiency during this stage is 100 %. The concentration of pollutant which marks the change between the kinetic and the mass transport (limit concentration) depends on the fluid-dynamic conditions and on the particular pollutants. As the waste composition changes continuously during a batch treatment, this value is not constant and, hence, accurate predictions in an actual treatment are usually difficult. Carbon dioxide is the sole final product in the electrochemical treatment of the tested compounds with BDD anodes. The main intermediates are carboxylic acids C_4 and C_2. In addition to the waste characteristics, operating conditions play an important role in the electrochemical oxidation of organic wastewaters.

Since direct oxidation processes remain almost unaffected by temperature, this fact must be explained in terms of the presence of inorganic electrogenerated reagents. The oxidation carried out by these redox reagents is a chemical reaction and, consequently, its rate normally increases with temperature. This fact confirms that the oxidation processes proposed [19] can be carried out either at the electrode surface or through electrogenerated reagents – mainly hypochlorite and peroxodisulphates. However, new organic intermediates are not formed with increasing temperature, indicating that the process mechanisms do not vary with temperature. The global oxidation rate of the electrochemical treatment of phenolic compounds does not depend on the pH, at least in the experimental conditions studied.

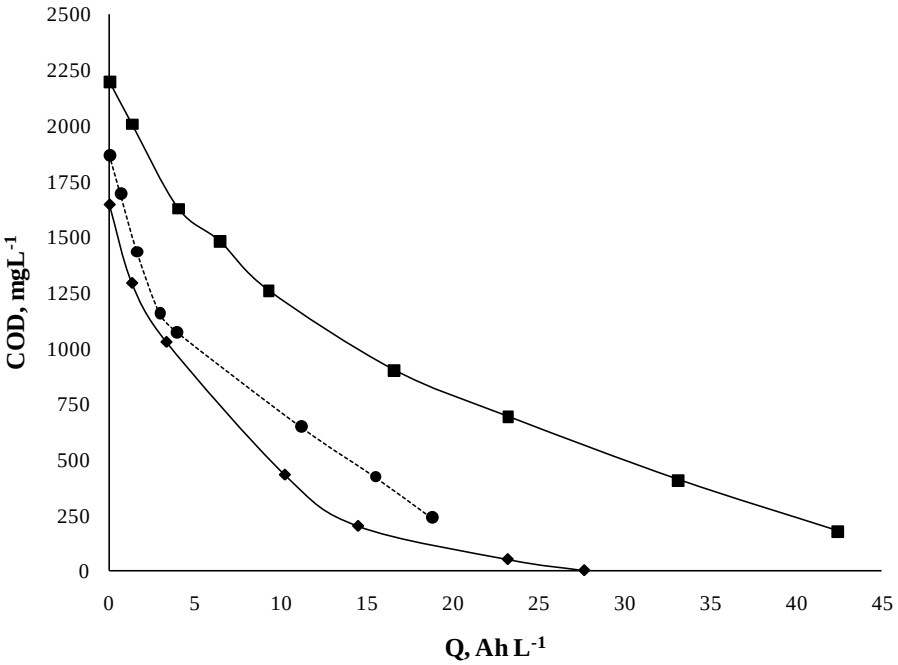

Figure 1. Typical variation of COD for phenol compounds in different experimental conditions. ■ COD_0= 2250 mg L^{-1}, pH 2 and j: 60 mA cm^{-2}; ◆ COD_0= 1650 mg L^{-1}, pH 2 and j: 60 mA cm^{-2}; ● COD_0= 1850 mg L^{-1}, pH 12 and j: 60 mA cm^{-2}.

In this way, Figure 2 shows the correlation between COD obtained experimentally and COD predicted by mathematical model for all experiments used in this work. In this figure, taking into account the large number of data, they were clasified as funtion of the organic pollutant (independently of the experimental conditions used). As can be observed from the Figure, the percentual relative error between the COD values obtained experimentally and with mathematical model for the six phenol compounds is around 33.731 % and a correlation is 0.975. There are identified three areas (noted as 1, 2 and 3) where the points are situated out of the cross bar. Consequently, the mathematical model is good from two points of view: it quantifies chemical laws which govern the process and the accuracy of the results is satisfactory. However, the results of the classical model can be improved with a neural network which corrects the errors by modeling the residuals of the phenomenological model.

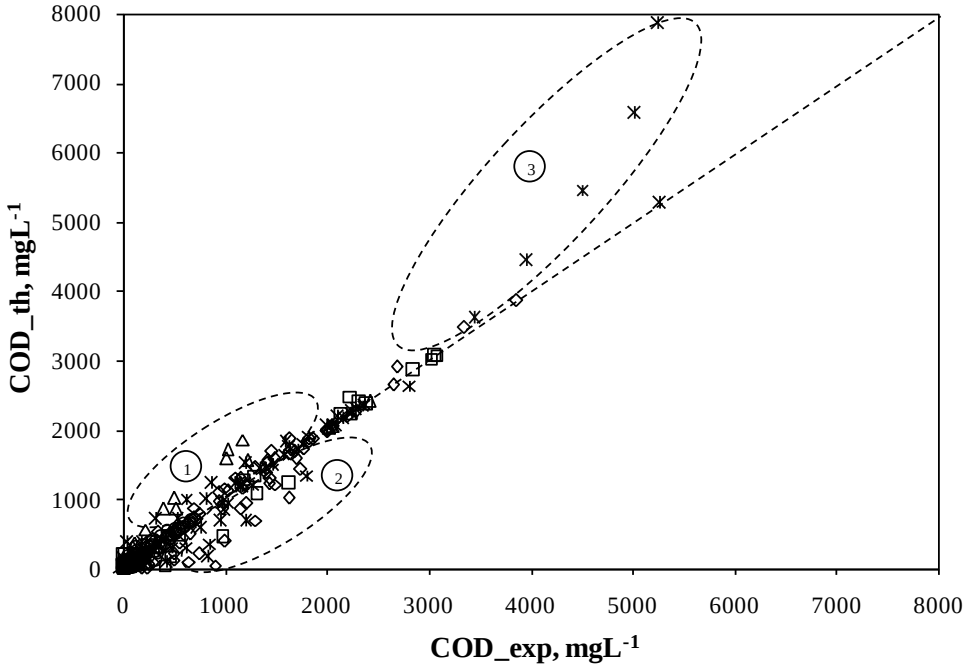

Figure 2. Correlation between COD obtained experimentally (COD_exp) and with mathematical model (COD_th) for the six phenol compounds considered. ◇ Phenol; □4-Chlorophenol; △2,4-Dichlorophenol; ✕2,4,6-Trichlorophenol; ∗4-Nitrophenol and ○ 2,4-Dinitrophenol. Initial COD: 45–5300 mg dm^{-3}; pH 2 and 12; T:15–60 ºC; j: 15–60 $mAcm^{-2}$.

3.2. Hybrid approach based on neural network and phenomenological model

One major problem in the development of neural network model consists in determination of the network architecture, *i.e.* the number of hidden layers and the number of neurons in each hidden layer. Firstly, potentially good topologies must be identified. Nevertheless, no good theory or rule accompanies the neural network topology that should be used and trial-and-error is still required. This is done by testing several topologies and comparing the prediction errors. Lower errors indicate potentially good architectures, *i.e.* neural network topologies with chances to train well and to output good results.

For our case study, 420 available experimental data were divided into training (90 %) and validation data (10 %). The following seven parameters were chosen as input variables for the neural models: temperature (15 - 60°C), initial COD (with the range: 45 – 5300 mg L^{-1}), pH (2 - 12), current density (j, 15 – 60 mA cm^{-2})□□charge (Q, 15–60 Ah L^{-1})□□□types of chlorine phenol compound, codified as 1 (4-chlorophenol), 2 (2,4-dinitrophenol) and 3 (2,4,6-trichlorophenol) and type of nitrophenols compounds, codified depending of nitro functions with the values of 1 (4-nitrophenol) and 2 (2,4-dinitrophenol). The final COD was the output of the network (COD_q).

Since phenomenological model does not give accurate results (Figure 2), one possibility to improve it is to correct its errors with a neural network. The structure of the hybrid model, in which the phenomenological model and the neural network model are coupled, is presented in Figure 3.

According to the hybridization mechanism, theoretical values for COD provided by the phenomenological model are compared with the experimental ones and the differences constitute the

residuals that were considered the outputs of the neural network model. The inputs of the neural network are the same parameters as for classical model (temperature, initial COD, pH, current density, charge□□□types of chlorine and phenol/nitrophenols compounds).

Table 1 presents the best neural networks for each types considered for the hybrid model (MLP, GFF, MNN and JEN). Also, different transfer functions for hidden and output layers, in homogeneous or heterogeneous combinations, were tested.

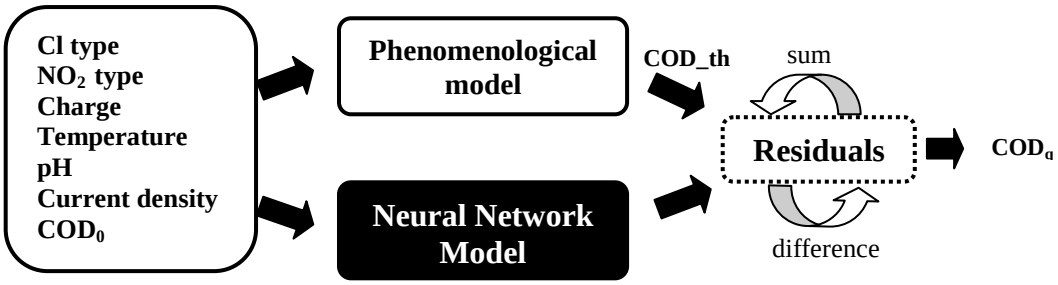

Figure 3. Structure of the hybrid model composed of phenomenological model and a neural network.

In the training phase, an average relative error of 7.98 % and a correlation between experimental and predicted data of 0.9992 were registered for the best model, MLP(7:25:20:1), a multilayer perceptron with 7 inputs, 2 hidden layers with 25 and 20 neurons, respectively, and 1 output.

Table 1. The best neural networks to be included into the hybrid model.

Network type	Activation function	Training stage		Validation stage	
		Correlation	Error	Correlation	Error
MLP(7:25:20:1)	Tanhaxon	0.999232	7.979923	0.998203	8.9389965
MLP(7:25:20:1)	Tanhaxon-Sigmoidaxon-Axon	0.998609	13.94491	0.99672	10.59845
GFF(7:25:20:1)	Tanhaxon	0.998228	24.14195	0.897901	23.181836
MNN(7:50:40:1)	Tanhaxon	0.998003	24.14195	0.800197	27.244757
JEN(7:25:20:1)	Tanhaxon	0.999954	34.78001	0.88031	63.202753

Relative errors were calculated using Eq. (6) where indexes *exp* and *hybrid_model* denote experimental and hybrid model values.

$$E_r = \frac{COD_{exp} - COD_{hybrid\_model}}{COD_{exp}} \cdot 100 \quad (6)$$

A key issue in neural network based process modeling is the robustness or generalization capability of the developed models, *i.e.* how well the model performs on unseen data. Thus, a serious examination of the accuracy of the neural network results requires the comparison with experimental data, which were not used in the training phase (previously unseen data). For the validation stage, the average relative error of about 8.93 % and the correlation value of 0.998 obtained with MLP(7:25:20:1) reflect a satisfactory capacity of generalization. Consequently, for the hybrid model, MLP(7:25:20:1) with Tanhaxon as activation function for hidden and output layers is chosen because of the good performance and the simplicity of this type of neural network.

It is known that sometimes heterogeneous combinations of transfer functions can provide better performance than using one single function [6]. The first three rows in Table 2 correspond to neural modeling accomplished with an individual MLP network having homogeneous and heterogeneous transfer functions and with stacked neural network whose output is obtained as a weighted sum of the individual outputs.

The best results were obtained in the last case and correspond to a relative error in validation phase of 5.8 % and a correlation of 0.999 [6]. Taking into account the accuracy and possibility to develop and manipulate the models, the best alternative for the electrolysis process seems to be the hybrid model, even the relative error is superior to the error of the stack

Table 2. Comparison between performance of different models for electrolysis of phenols compounds [6].

Model	Relative error at validation stage %	Correlation
Individual neural network (MLP) with homogenous transfer function (Tanhaxon)	10.957	0.997
Individual neural network (MLP) with heterogenous transfer functions (Tanhaxon – Sigmoidaxon – Axon)	7.261	0.999
Stacked neural network	5.823	0.997
Phenomenological model	33.731	0.975
Hybrid model	8.942	0.998

A comparison between the three available models (phenomenological, hybrid and stacked neural network models) is made in Figure 4 for the training phase. One can observe that the two models based on neural networks are in good agreement with experimental data

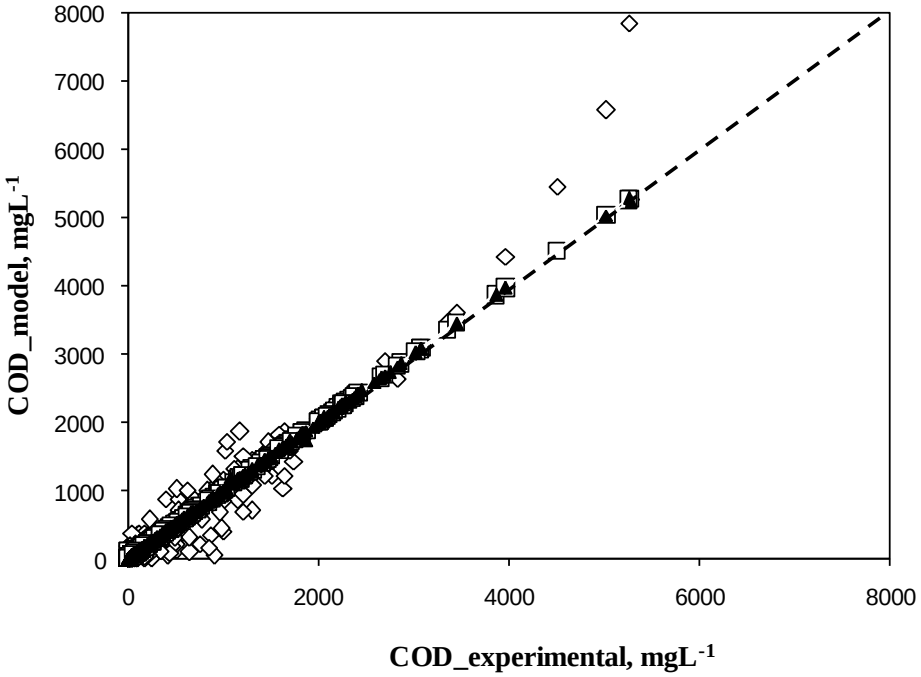

Figure 4. Comparison between predictions of phenomenological, hybrid and stacked neural network models for the training stage. ◇ Theoretical model; □ Hybrid model and ▲Staacked NN model.

Finally, Figure 5 shows the validation phase, where the best results are obtained with hybrid model. Taking into account the accuracy and possibility to develop and manipulate the models, the best alternative for the electrolysis process seems to be the hybrid model, even the relative error is superior to the error of the stack.

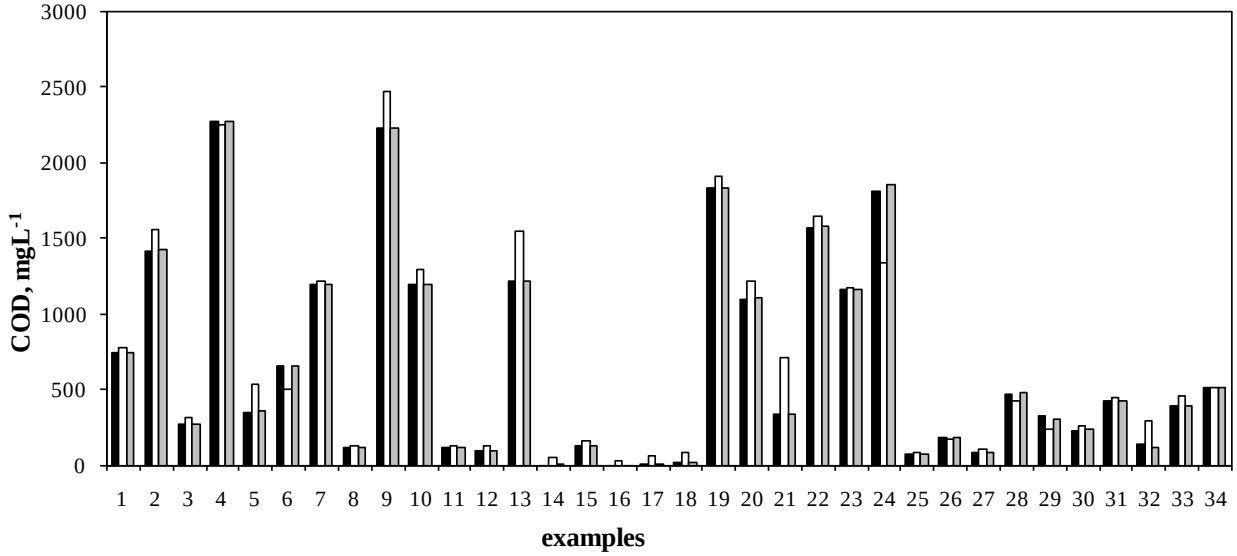

Figure 5. Comparison between experimental data and predictions of phenomenological and hybrid models for the validation stage**.** ■COD exp; □ COD math model and ■ COD hybrid model.

4. CONCLUSIONS

A hybrid approach based on a mathematical model and a neural network is developed in order to improve the model quality of the electrolysis process of a series of phenolic compounds.

The organic nature of the wastewater compounds has a high influence on the efficiency of electrochemical oxidation process. The electrochemical oxidation was used to treat succesfully phenolic aqueous wastes, CO_2 being the main reaction product from the electrolysis process based on boron doped diamond.

A mathematical model was designed to predict COD as a function of experimental conditions. As main disadvantage of this model could be mentioned the high percentual error (~33%) that is dependent on the phenol compound type. This error could be explained in the context of the existance of oxidizing compounds, including persulphates and hydrogen dioxide, also as a dependence of the waste composition and the operating conditions.

The hybrid model includes the mathematical model and a neural network which has the role to correct the residuals of the phenomenological model. There were tested several neural network types (MLP, GFF, MNN and JEN), with homogenous and heterogenous transfer functions. The best results were obtained designing a MLP neural network with a tangent hyperbolic axon as transfer functions, used along with the phenomenological model, in a hybrid combination.

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