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Modeling Methodology Based on Neural Networks Applied to an Electrochemical Treatment Wastewater Process

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Abstract

This paper presents different methodologies of modeling based on simple and stacked neural networks with homogenous and heterogeneous transfer functions. They were applied to an electrolyses process of wastes polluted with phenol compounds, allowing to predict with a good accuracy the chemical oxygen demand as a function of the initial characteristics (pollutant concentration, pH), operation conditions (temperature, current density) and electrolysis time. Global errors of the training stage for the stacked model were under 3 % and those of the validation stage were under 4 %. The developed neural models could be applied in industry to determine the required treatment period, to obtain the discharge limits in batch electrolyses processes, as a first step in the development of process control strategies.

Key words: *stacked neural networks, transfer functions, electrolysis process, wastewater treatment.*

Introduction

Generally, a phenomenological model involves many difficulties when a limited knowledge about it is available. Artificial neural networks are a representative artificial intelligence technique that can be used for classical process modeling. They are one of the most popular tools with applications in areas such as pattern recognition, classification, process control, optimization [1-3].

Neural networks have many advantages: the possibility to be applied on complex non-linear processes, the ease in obtaining and using neural models or the possibility to substitute experiments with predictions. On the other hand, the disadvantages seem to be related to obtaining a low-error neural network that models experimental or operational history data.

The idea of combining different neural network models is based on the premise that different networks capture different aspects of process behavior and aggregating this information should reduce uncertainty and provide more accurate predictions. Stacked neural networks have been successfully used for the inferential estimation of many chemical processes [4, 5]. The aggregation process of the individual neural networks can be performed in different ways. The most frequent situation assumes the weighted combination of the neural network outputs. In another example, individual neural networks are arranged in a cascade and they are sequentially applied on the sub-intervals of the considered domain [6]. Hybrid models, composed of a

simplified phenomenological model, and one or several neural networks represent another possibility to improve the performance of the neural model [7].

Electrochemical wastewater treatment processes are becoming a very interesting choice for the treatment of industrial wastes flows, especially in the cases where the characteristics or the concentration of pollutants advice against the use of biological or incineration technologies. Recently, many works have been published concerning the use of electrolyses in the treatment of synthetic wastewaters [8-10]. Within these technologies, the use of diamond anodes has given an important advantage due to the great removals of Chemical Oxygen Demand (COD) and to the great energy efficiencies of these processes.

The main goal of the present paper is to emphasize the option of using individual or stacked neural networks, with different architectures and different transfer functions, to predict the evolution of COD as a function of others parameters involved in an electrochemical wastewater treatment.

Experimental details

In order to obtain operational data sets, 420 available experimental data were taken into account for 6 phenol compounds: phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 4-nitrophenol and 2,4-dinitrophenol [8,11,12]. They were divided into training (90 %) and validation data (10 %). Different concentrations were considered and the pH was kept constant by the continuous introduction of sulphuric acid (or sodium hydroxide) to the electrolyte reservoir. The cell potential was constant during each electrolysis, indicating that appreciable deterioration of the electrode or passivation phenomena did not take place.

Chemical Oxygen Demand (COD) was determined using a HACH DR2000 analyzer. The electrolysis of each organic pollutant was carried out in a single-compartment electrochemical flow cell [12]. Diamond-based material was used as the anode and stainless steel as the cathode. The electrolyte was stored in a glass tank 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.

To develop the neural network models, 7 parameters were considered as inputs variables: time (minutes), temperature (15 - 60°C), initial COD (with the range: 45 – 5300 mg dm^{-3}), pH (2 - 12), current density (j: 15 – 60 mA cm^{-2}), 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 as 1 (4-nitrophenol) and 2 (2,4-dinitrophenol) in order to determine the final COD as the output of the network (COD_q).

Results

Feedforward neural networks with different topologies were trained and their performances were evaluated based on means squared error (*MSE*) and correlation between experimental data and network predictions (*r*). The best network found by this trial and error method was MLP(7:25:20:1) – multilayer perceptron with 7 neurons in the input layer corresponding to the 7 input variables, 2 hidden layers with 25 and 20 neurons, respectively, and 1 neuron in output layer for the final COD. The transfer function applied to all the hidden layers and the output layer was the hyperbolic tangent. Figure 1 presents some predictions of this network versus the training (experimental) data set.

As it can be observed from Figure 1, the complete removal of the soluble organic compounds contained in the waste is obtained. Likewise, it is shown that the electrolysis leads to the generation of a low concentration of intermediates during the first stages of the treatment and that they are finally oxidized, leading 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 concentration. As the waste composition continuously changes during a batch treatment, this value is not constant and hence accurate predictions in an actual treatment are usually difficult. In this context, the use of neural networks can help to model this system in a more accurate way.

In the training phase, an average relative error of 1.83 % and a correlation between experimental and predicted data of 0.9998 were recorded. Figure 2 presents some results obtained in the validation stage, with an average error of about 8 % and a correlation value of 0.994.

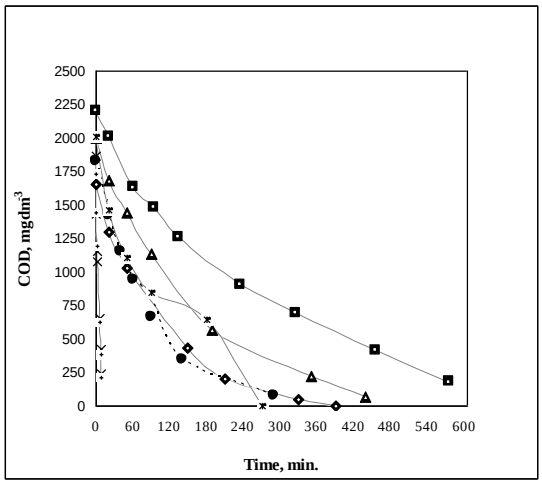

Fig. 1. Training stage for MLP(7:25:20:1) with different parameters (pH and current density).

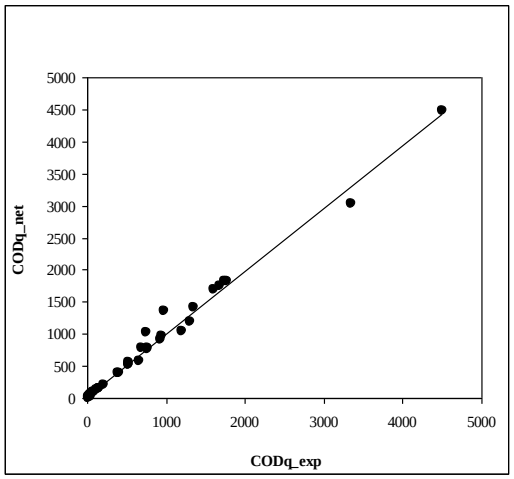

Fig. 2. Validation stage of MLP(7:25:20:1).

Choosing adequate transfer functions can contribute to the optimization of the neural model. Many series of MLP networks were generated, considering hyperbolic tangent as the best transfer function on the first hidden layer and using eight different transfer functions for the second hidden layer and for the output layer: 1- TanhAxon (hyperbolic tangent), 2 – SigmoidAxon (unipolar sigmoid), 3 – LinearTanhAxon (piecewise linear approximation to hyperbolic tangent), 4 – LinearSigmoidAxon (piecewise linear approximation to unipolar sigmoid)**,** 5 – SoftMaxAxon (function with outputs sum to 1, used for classification, postprocessor to translate the network outputs into probabilities), 6 – BiasAxon (linear axon with adjustable slope and adaptable bias), 7 – LinearAxon (linear axon with adaptable bias), 8 – Axon (simplest axon, identity transfer function). Figure 3 presents the performance of the neural networks obtained with different combinations of transfer functions.

The best combination of the transfer functions was TanhAxon-SigmoidAxon-Axon for the two hidden layers and the output layer, respectively, with MSE = 0.00023998 in the training phase and 7 % average error of validation stage (Figure 4). Consequently, an adequate combination of the transfer functions in the neural model represents a way of improving the robustness capability of the network.

Another step for obtaining a better performance within the modeling strategy consists in using stacked neural networks. Three different neural networks were trained and aggregated and their outputs were weighted. Figure 5 presents the neural networks developed and combined in the stack, with percent error and correlation recorded in the training phase. These neural networks

were: GFF(7:25:20:1) (Generalized Feed-Forward neural network) with TanhAxon-SigmoidAxon-Axon transfer functions for the two hidden layers and the output layer, MLP(7:25:20:1) with the same combination of the transfer functions and MLP(7:25:20:1) with a single type of transfer function, TanhAxon. The smallest validation error obtained was 5.8227, as compared to previous modeling techniques, using the weights 0.71, 0.16 and 0.11, respectively (Figure 6).

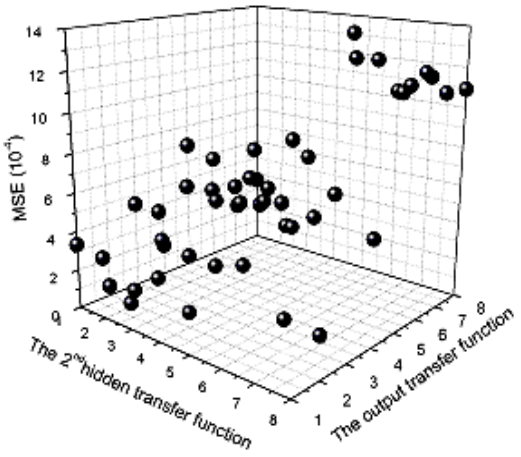

Fig. 3. Performance of models using different transfer functions.

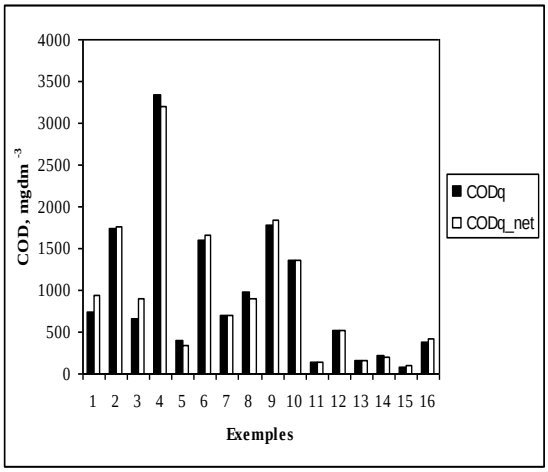

Fig. 4. Validation stage for the best combination of the transfer functions for MLP(7:25:20:1).

Consequently, the most appropriate modeling strategy in our case study is the one which aggregates individual neural networks and uses a TanhAxon-SigmoidAxon-Axon transfer function combination. Such a model can be used to make accurate predictions under different reaction conditions and it offers the possibility of substituting experiments that are time and material consuming.

The neural networks were trained with *NeuroSolutions* and the aggregation process was conducted with an original application (*Stacked Neural Networks*) designed with a graphical user interface (Figure 7). The following steps are necessary to obtain the results for the stack neural network: selecting the neural networks, selecting the weight of each network, specifying the dataset used for predictions and computing the actual test.

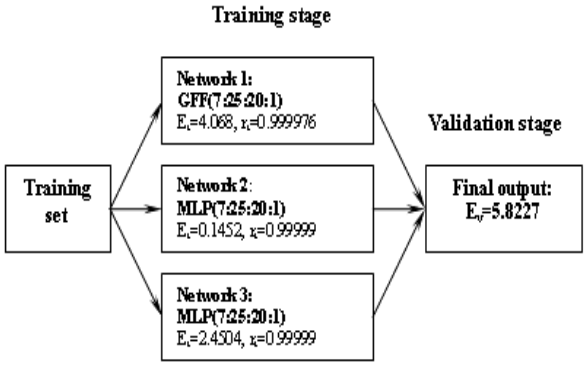

Fig. 5. The strategy of modeling based on stacked neural networks.

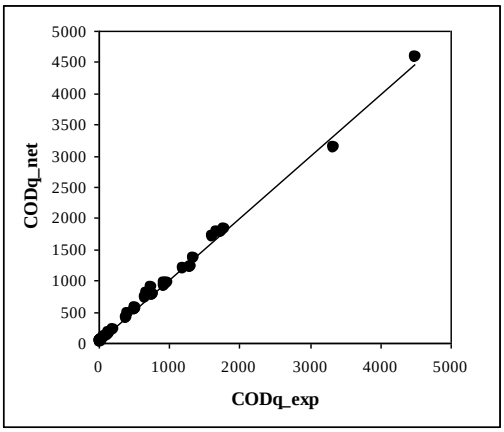

Fig. 6. Validation results of the stacked neural networks.

Figure 8 shows the results of a validation trial applied to a *real wastewater case* carried out with the best neural network modeling (Figure 5), in order to justify and validate the variation of

COD during the treatment of wastewater on boron doped diamond electrodes. The wastewater is the effluent of a fine-chemicals plant which consists of an aqueous solution of solvents with a high concentration of aromatic compounds coming from the raw materials, intermediates, and products of different processes of the plant. Two experimental datasets with pH values of 2 and 12 were taken into account. The average error between the experimental and predicted COD was around 4.92 %. Hence, the COD variation in the real electrochemical oxidation of polluted wastes does not substantially differ from that obtained for other synthetic wastes, previously tested with the model. Furthermore, the modeling methodology developed in this work could be applied in order to control a real electrochemical process.

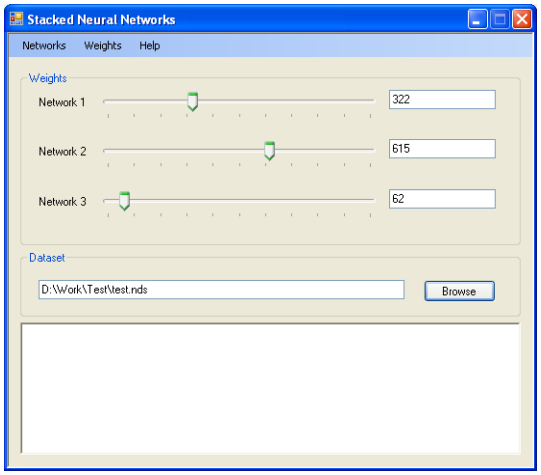

Fig. 7. Main program window

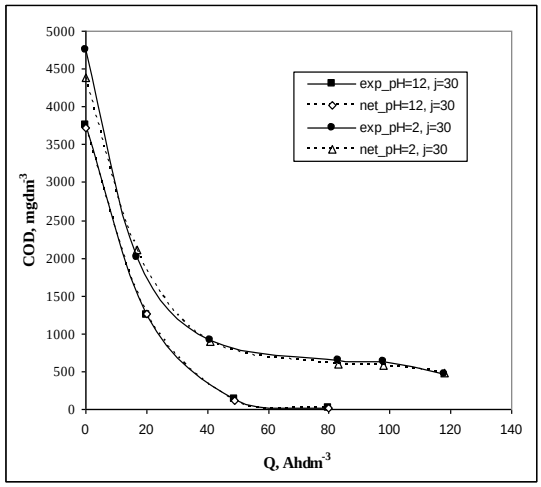

Fig. 8. Supplementary predictions obtained with the stack neural network.

Conclusions

The electrochemical oxidation with conductive diamond electrodes can be used to treat phenolic aqueous wastes. The complexity of the oxidation mechanisms involved in this process and the variety of intermediates generated during the process makes it difficult to use a phenomenological model for controlling purpose. In this way, artificial neural networks appear as a promising alternative tool for classical process modeling. Thus, in this work, the development of neural networks to model the electrolyses of wastes polluted with phenols compounds was carried out. Different strategies based on individual neural network architectures and stacked neural networks were evaluated using different transfer functions. Feed-forward neural networks (MLP or GFF) were designed for the whole set of experimental data or for some subsets of data. Individual networks were also combined in stack, weighting the outputs of the networks. Trying different combinations of transfer functions in hidden and output layers proves to be an option to improve the modeling results. Good predictions are obtained in the validation phase, so the neural networks give a very good representation for the wastewater treatment process analysis.

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Metodologie de modelare bazată pe rețele neuronale aplicată unui proces de tratare electrochimică a apelor uzate

Rezumat

Această lucrare prezintă diverse metode de modelare bazate pe rețele neuronale simple și agregate în stive, cu funcții de transfer omogene sau eterogene. Modelările au fost aplicate unui proces de electroliză a unor ape uzate pe bază de compuși fenolici. S-au obținut predicții precise pentru consumul chimic de oxigen, acesta fiind determinat funcție de caracteristicile inițiale (concentrația poluantului, pH), condițiile de operare (temperatură, densitate de curent) și timp de electroliză. Erorile medii ale etapelor de antrenare și validare pentru modelul stivă au fost sub 3%, respectiv 4%. Modelele neuronale obținute pot fi aplicate proceselor industriale de electroliză, acesta constituind un prim pas în dezvoltarea strategiilor de conducere automată a procesului.