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Treatment of Leachate by Oxidative Process via Fenton and Modeling of the Process by Neural Networks

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Abstract

This paper aims the treatment of leachate in a reactor in batches using the advanced oxidation process *via* Fenton, allowing partially oxidize organic compounds and making them biodegradable, being removed by filtration or sub-

sequent biological treatment. This technique allows to verify the satisfactory operating conditions for greater removal efficiency of both organic load as nutrients. The process was modeled via neural network of the kind feedforward and backpropagation. The best configuration to represent the relationship between the variation in chemical oxygen demand (network output layer) and the factors presence or absence of lime, time, pH, volume of hydrogen peroxide solution and concentration of Fe^{2+} (network input layer) was obtained with 12 neurons in the hidden layer and the tangent sigmoidal transfer functions. The correlation coefficients above 0.99 for the phases of training and simulation show the power of the generalization of neural model obtained.

Keywords: Leachate, Chemical oxygen demand (COD), Fenton, Modelling by neural networks, Advanced oxidation processes (AOP)

1 Introduction

One of the major problems faced by modern society is the resolution of the urban waste issue. With the intensification of the industrial process, combined with population growth and the consequent demand for consumer goods, human being has produced large quantities of waste, which most often are intended to landfills [1].

The leachate material, from landfills, may contain a large amount of recalcitrant organic matter (not degraded by microorganisms), where the group of humic acids is an important part of this material. Conventional methods used for the treatment of the leachate are based on physico-chemical processes (adsorption and flocculation) and biological agents that have a high purification efficiency. However, the contaminants are not degraded by physical and chemical processes, what necessarily implies in the generation of solid phases (sludge) highly contaminated. In the biological process (activated sludge), there is a need for long residence period (ranging from days to weeks) and low efficiency in the removal of colored compounds and recalcitrant [2], making its effectiveness quite discussed.

In this context, Advanced Oxidation Processes (AOPs) are presented as a satisfactory alternative to maximize the degradation of the leachate, because they are based on the generation of the hydroxyl radical (highly oxidizing) and may lead to complete mineralization of organic compounds (carbon dioxide formation and water). Briefly, several AOPs are divided into two groups: Homogeneous and Heterogeneous Processes. The first occurs in a single step using ozone and H_2O_2 or Fenton's reagent (H_2O_2 mixed with Fe^{2+} salt) as hydroxyl radical generators. The second one uses semiconductors as catalyzers (titanium dioxide, zinc oxide, etc.) [3]. The use of UV radiation and the semiconductor properties of the catalyzer allow the formation of hydroxyl radicals and the subsequent oxidation of the effluent.

According [4], [5], the final disposal method of solid waste for landfill continues to be widely accepted and used because of its economic advantages.

Comparative studies of various solid waste disposal methods (landfill, incineration, composting, etc.) have shown that the most economical method is the use of landfills. Through this method, there is the decomposition of waste under controlled conditions until its eventual transformation into relatively stable and inert matter in the environment.

This project aims the treatment of leachate in a reactor in batches using the advanced oxidation process *via* Fenton, allowing partially oxidize organic compounds and making them biodegradable, being removed by filtration or subsequent biological treatment. This technique allows to verify the satisfactory operating conditions for greater removal efficiency of both organic load as nutrients.

1.1 Advanced Oxidative Processes (AOPs): General approach

Although the Advanced Oxidation Processes make use of different reaction systems, they have the same chemical characteristic: production of hydroxyl radicals. The hydroxyl radicals correspond to reactive chemical species of extraordinary capacity, with poor selective activity and a potential of 2.8 V, attacking most organic compounds having kinetic constants of the order of 106-109 M^{-1} s^{-1}. Due to its high reactivity, the hydroxyl radicals can cause total mineralization of organic compounds into harmless compounds such as CO_2 and water. Since AOPs can be classified into homogeneous or heterogeneous systems, •OH radicals are generated with or without UV irradiation. Among the homogeneous systems, it can be mentioned those that involve the use of hydrogen peroxide and the catalytic decomposition of hydrogen peroxide in acidic medium - Fenton reaction or photo-Fenton [6]. Among the heterogeneous systems, it can be mentioned those which are used ozone and semiconductors such as TiO_2 and ZnO (photocatalysis) [6]. In Fenton process, hydrogen peroxide is added to the effluent in the presence of ferrous ion salt, generating strong oxidizing species, among which stands out the •OH. The mechanism involved in the generation of hydroxyl free radicals in the Fenton conventional process, depending on the concentrations of Fe^{2+} and H_2O_2, presents high kinetic constants (53-76 M^{-1} s^{-1}). In the presence of organic compounds, hydroxyl radicals can attack the organic load in four ways: radical addition, hydrogen abstraction, electron transfer and combination of radicals. The organic radicals generated R, R-OO and R-O can form, with their pairs or randomly, relatively stable molecules or react with iron ions. This production of organic radicals can continue to react with the hydroxyl and O_2 radicals, until additional decomposition or complete mineralization in water and carbon dioxide.

Fenton reagent is currently used to treat a wide variety of toxic organic compounds that do not respond to biological treatments. It can be applied to a wide variety of waste waters or in the remediation of contaminated soils, with various effects [4].

[7] analyzed the technical practicability of the treatment of landfill leachate using Fenton's reagent. The tests were run on the Landfill of Cachoeira Paulista,

where the process was carried out in batch, with 1000 L production capacity, using a simple mixture reactor. The results showed high efficiency in the removal of organic pollutants, in which the removal of DQO were about 61%, with a higher removal reached of 75%, which required the smallest amount of reagent and stirring shorter period and, consequently, lower cost of operation.

[8] studied the application of photo-Fenton process in the leachate generated in the city of Colmenar Viejo, Madrid-Spain, where it was obtained the removal of organic content was 75% of TOC and 80% of DQO by using an artificial light at 400W. Due to the inherent characteristics of the reaction process involving the irradiation of light, there are few studies with samples containing high concentrations of soluble solids and high value of turbidity and color. This scientific consensus, although pragmatic, have been changed with the publications, even in small numbers, with samples that are constituted by the same physical and chemical characteristics.

[9] conducted a study on the milky effluent from Danone in Guaratinguetá-SP. This effluent had physicochemical characteristics similar to leachates, using the photo-Fenton reaction with an artificial light to assist in the degradation of the organic components, obtaining removal organic burden rate of 90% for TOC and 92% COD.

1.2 Neural Networks

A neural network is a massively parallel distributed processor that has a natural propensity for storing experimental knowledge and making it available for use. In a neural network, knowledge is acquired by the network through the process of learning and the weights of the connections between neurons, known as synapses, are used to store knowledge [10].

[11] emphasized the difficulty of mathematical modeling due to the chemical complexity of advanced oxidation processes and, therefore, neural networks could be used in the mathematical modeling of the effluent degradation, due to its simplicity of simulation, prediction and modeling. The advantages of neural modeling involves the fact that the description of the phenomenon of degradation is not necessary and a shorter time is required for the development of the model if compared to traditional mathematical models. Along similar lines, [12] used a feed-forward backpropagation neural network for prediction of the critical point of addition of hydrogen peroxide in the azo dyeing process, using UV/H_2O_2.

In most designs, these connections are associated with weights that store the knowledge represented in the model and serve to balance the input received by each neuron in the network. Problem solving with neural network initially goes through a learning phase, where a set of examples is presented to the network, which automatically extracts the necessary features to represent the information provided. These characteristics are then used to generate answers to the problem.

[13] reports that the complexity of the photochemical mechanism leads to big difficulties in the determination of kinetic models. The hydroxyl radical is not selective, making difficult the description of kinetic models in a simple way.

In this study, the neural network used was a feedforward-like network, consisting of three layers (input, hidden and output). The feedforward neural network fit criterion using back-propagation algorithm was used in order to minimize the mean square error for training sets, validation and test. The performance of the feedforward network [14] can be defined according to the Equation (1).

$$\overline{Y_i} = f_0\left[\sum_{j=1}^{h_n} W_{0j} * f_h\left(\sum_{i=1}^{m} WH.X_i + b_j\right) + b_0\right] \quad (1)$$

In the Equation (1), WH_{jj} represents the weights between the j-th input and the j-th hidden neuron, m is the number of input neurons, W_{oj} represents between the weights j-th hidden neuron and the output neuron, f_h represents the activation function of the hidden neuron, f_o is the activation function of the output neuron, b_j is the bias of the j-th hidden neuron, b_o is the bias of the output neuron and h_n is the number of hidden neurons. In this notation, is explicit functional character of neural modeling. This way, it may be a predictive value in the functional or classification sense.

The basic objective of neural modeling is the minimization of an error function. In this development, the mean square error function is represented by Equation (2), in which N is the number of samples of the experiment.

$$MSE = \sum_{i=1}^{N} (Y_i - \overline{Y_i})^2 / N \quad (2)$$

2 Material and Methods

The first part of the study is the mounting of the reactor and the working methodology adjustments. Fenton reaction experiments were performed in borosilicate glass reactor manufactured by Adonex. A wood base affix the tubular reactor of 42 cm and 4 inches of internal diameter, with volumetric capacity of 4 L. The reactor consists of three entries, two on the same side situated in the points of 22 and 40 cm in height, for the entrance of the reagent or recycle, respectively; the other opposite at 5 cm height for aeration of the system. In the lower base of the reactor there is a tap to collect the treated effluent.

A metal band affix the reactor to a conical cover with polished escape on the top. This escape connects to the polished part of a glass tube with arc-shaped, which is attached to a plastic tube. This apparatus is designed to condense the foam formed, by the introduction of air, directly after it passes through the half of the arc at the top of the reactor, which condenses and returns to the process, avoiding loss of reagent and effluent.

It was developed a fractional factorial design sheet (2^{3-1}), with triplicate at the center point and random duplicates and the input variables were: amount of H_2O_2

(mL) (66.9; 83.5; 100.5), amount of Fe^{2+} (g/L) (15.9; 30.19; 45.29) and pH (2; 3; 4), according to Table 1. The response variables in this planning were the degradation percentages of the total organic carbon (TOC) and chemical oxygen demand (COD) in leachate degradation.

The aeration system is made of porous stone, that with bubbling, promotes the agitation of the reaction medium. The reactor can be operated in batch, with recycle or continuously system and for the last two, an adaptation is performed by a 3-way glass piece set in the metal band, which function is flattening the desired system operation volume. The description of the reactor is shown in Figure 1.

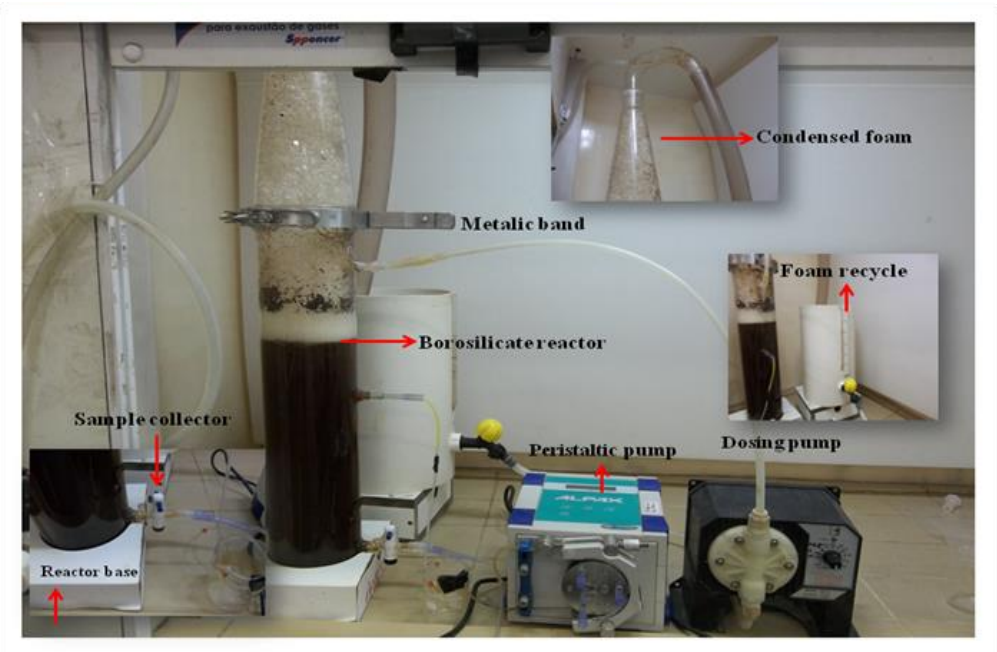

Figure 1- Mounting scheme reactor

Table 1 – Control factors of treatment levels of leachate from the landfill of Cachoeira Paulista – SP

FACTORS	LEVEL Low (-1) Middle (0) High (1)
1- Amount of H_2O_2 (mL)[1]	66,9 83,7 100,5
2- Amount of Fe^{2+} (g/L)[2]	15,9 30,19 45,29
3- pH	2 3 4

[1]$[H_2O_2]$ = (25%, 66,9 mL; 50%, 83,7 mL;excess 100,5 mL) [2]$[Fe^{2+}]$ = 1g L^{-1}

2.2 Analytical characterization of leachate *in natura* from the landfill of Cachoeira Paulista-SP

The characterization of leachate is being carried out according to the most relevant physico-chemical aspects, such as chemical oxygen demand (COD) ,biochemical oxygen demand (BOD), total organic carbon (TOC), fixed and volatile solids, organic and ammoniacal nitrogen, phenol, residual peroxide, oils and greases, color, pH and turbidity. The physical, chemical and biological characteristics of the leachate depend on the type of grounded residue, decomposition degree, climate, season, age of the landfill, profundity of the grounded residue, type of landfill operation, and so on. Therefore, the composition of the leachate can vary considerably from one location to another, but also in the same location between different seasons [6]. Thus, it becomes necessary to obtain more information about a particular leaching under study, by correlating their physical and chemical characteristics and with the processes of treatment involved.

The Table 2 presents some of the results of physico-chemical analysis of the leachate *in natura* from Cachoeira Paulista-SP and disposal values permitted by legislation set out in Article 18 - CETESB and CONAMA. The results found for the amount of COD, 4541.24 mg/L, is considered high, but it must be taken into consideration the factors related to the types of residues, climate and the form of final disposal of residues.

Table 2- Values of analytic parameters of leachate from the landfill of Cachoeira Paulista-SP

Parameters	Values	CETESB Article 18	CONAMA 357/05 and 430/11
DQO (mg O_2/L)	4541,24	-	-
DBO_5 (mg O_2/L)	-	Up to 60 or minimum removal of 80%	Minimum removal of 60%
COT (mg C/L)	1471,11	-	
Ammoniacal nitrogen (mgN-NH_3/L)	1262,49	-	20
Organic nitrogen (mg N_{org}/L)	11,49	-	-

Table 2- (Continued): Values of analytic parameters of leachate from the landfill of Cachoeira Paulista-SP

Phenol (mg/L)	164,34	-	-
Residual peroxide	0	-	-
Oils and greases (mg/L)	726	20	50
Color (Pt-Co/mg/L)	5711,41	-	75
pH	9	5,0-9,0	5,0-9,0
Turbidity (NTU)	302	40	100

(-) There is no value

The pH of the leachate undergoes large variations depending on the residues degradation phase. Alkalinity may occur due to the presence of bicarbonates, carbonates or hydroxides and represents the ability of the medium to resist possible variations of pH. Regarding oils and greases, there is a limit established by federal law. Mineral oils up to 20 mg/L and animal and vegetable oils 50 mg/L^{-1}. The value found for the analyzed leachate is above the maximum allowed limit. For parameters without limitation of maximum concentration, there is a marked change in the ammoniacal nitrogen parameters, phenol, oils and greases and turbidity.

2.3 Procedure related to the neural model

A feedforward backpropagation network that mapped a multi-dimensional space was implemented and the independent variables were: presence or absence of lime, time (min) pH, volume of hydrogen peroxide solution (mL) and Fe^{2+} concentration (g/L). The output variable Δ_{DQO} represents the decrease of COD calculated by an equation, which COD_0 is the oxygen chemical demand of leachate *in natura*, and COD_t is the content of COD after t minutes of treatment. In the proposed neural model, neurons of the input layer represent the independent variables or input variables and the output layer neuron represents the dependent variable ΔCOD.

$$\Delta COD = \frac{COD_o - COD_t}{COD_o} x100 \quad (3)$$

The Figure 2 shows the structure of the neural model applied to the Fenton oxidative process, where we can see the representative neurons of the input layer and the output layer of the neural network.

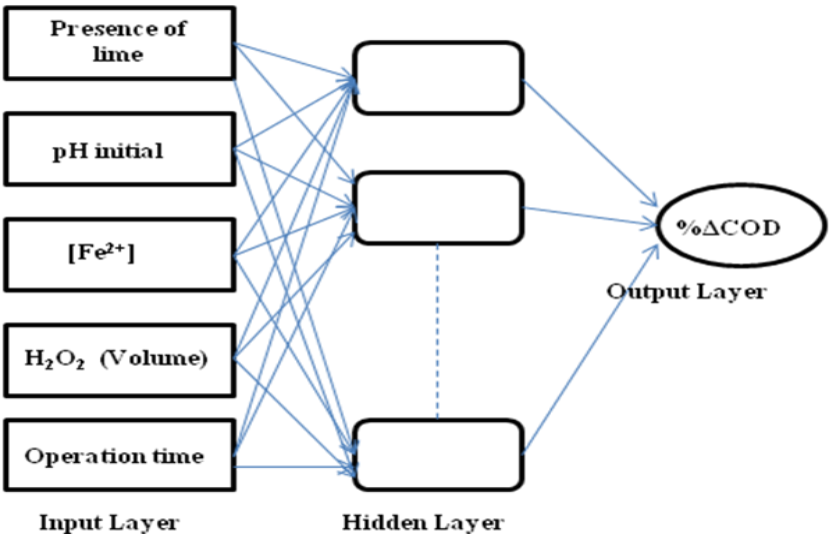

Figure 2- Example of Feed Forward Neural Network Model applied to Oxidative Advanced Process

During the network training process, various settings as to the number of neurons in the hidden layer were carried out. Among the results, it was chosen the configuration that worked with twelve neurons in the hidden layer because it was the one with the best correlation coefficient for the training groups and prediction. The computer environment used was network commands Matlab software, where the network parameters used can be checked.

```
n=input(enter the number of neurons in the hidden layer);
P=data(1:60,1:5); T=data(1:60,6); a=data(61:120,1:5); s=data(61:120,6);
[pn,minp,maxp,tn,mint,maxt]=premnmx(P',T');
[an,mina,maxa,sn,mins,maxs]=premnmx(a',s');
net=newff(minmax(pn),[n 1],{'tansig','tansig'},'traingdm')
net.trainParam.epochs=3000;net.trainParam.lr=0.9;
net.trainParam.mc=0.3;net=train (net,pn,tn);
y=sim(net,an); t=postmnmx(y',mins,maxs); plot(t,'r'); hold; plot(s);
title('Comparison between actual targets and predictions'
```

3 Results and analysis

A stage before the implementation of the neural network model and its optimization, data were transformed in a way that dependent and independent variables exhibited characteristics of particular distributions [3]. In this study, data were normalized to vary in the range [-1, 1], reducing possible influences of magnitude order of the input variables in neural modeling.

The data matrix was built using a set of 120 samplings, with collections with intervals of 10 minutes. From this set, 50% of the data were for the network training phase and 50% for prediction phase, in order to verify if the network behaved properly with known and unknown data, allowing to check the power of generalization of the neural model obtained. The Figure 3 shows a comparison between the training set and validation set of neural mode.

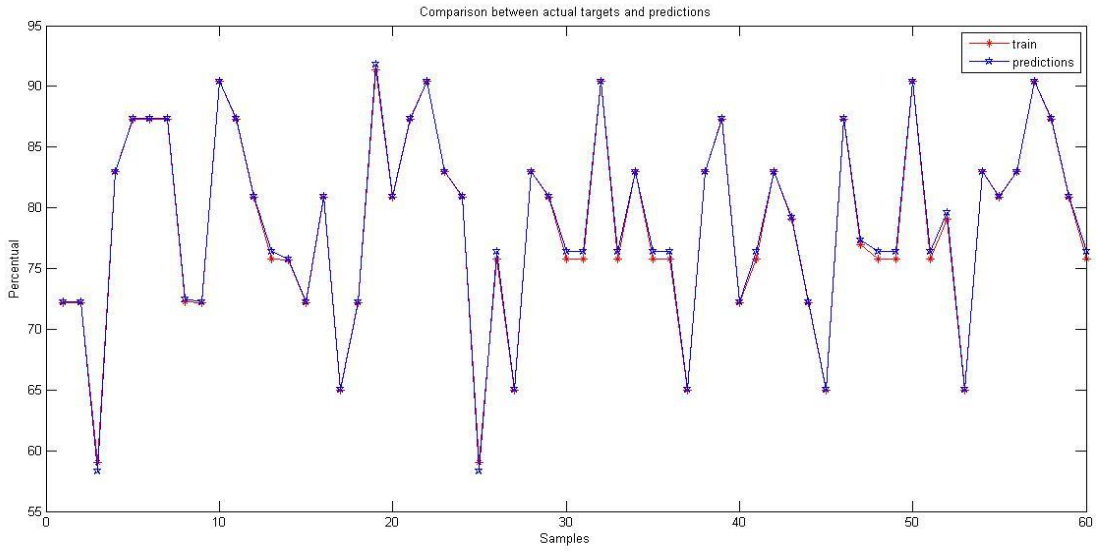

Figure 3- Comparison between actual targets and predictions

The optimal number of neurons in the hidden layer was determined based on the minimum value of MSE (Mean Square Error) of the training and prediction sets and in the linear correlation coefficients between these sets, varying the number of neurons from 1 to 25. The training phase showed a correlation coefficient between actual and predicted data with a value of 0.99937. In the prediction step, in which it is evaluated the generalization power of the network, for known data, it was obtained a correlation coefficient of 0.9958. The mean squared error of 0.1148 was obtained, calculated using the following equations:

$$d=[t-s]^2 \quad (4)$$

$$mse=mean(d) \quad (5)$$

$$mse = 0.1148 \quad (6)$$

4 Concluding Remarks

In this work, it was obtained a type feedforward backpropagation network with 3 layers that could predict the degree of degradation of *in natura* leachate using Fenton process. The configuration of the neural model which resulted in the lowest

MSE value used a tangent *sigmoid* transfer function in the hidden layer with twelve neurons and a linear transfer function (sigmoid tangent) in the output layer. The results predicted by the neural network were close to the experimental results with correlation coefficients above 0.99 for the training and prediction sets, showing the power of generalization of the proposed model.

The use of neural networks in the effluent degradation process by photo-oxidative processes can be coupled to statistical analysis, providing a form of mathematical modeling between representation of the model and computational time. The applicability techniques of neural networks and statistical analysis in addressing the problems of environmental issues, particularly in the prediction and analysis of effluent treatment processes must be highlighted.

Some characteristics of the neural models are presented as advantages in the analysis of effluent degradation processes, being remarkable the ability to model non-linear and complex processes such as photo-Fenton process, coated with non-linearities with the action of interfering in the analysis of environmental parameters such as COD. Random influence of ultraviolet radiation regarding environmental conditions is presented as a strong nonlinear factor on empirical data, with uncertain parameters that vary over time.

The use of models involving deterministic-character radiation procedures fills with mathematical complexity the photo-Fenton processes modeling, because they involve the energy equations solution, mass balance and thermal energy. In this sense, the neural model can easily be implemented in computer environments such as Matlab software. It must be emphasized that neural models are based on historical data of the process under study and that this knowledge base is not wasted and it can be inserted into new processes of modeling of the effluent, object of study of this paper. In particular, we could insert in the proposed model data of degradation process that would involve a new input variable, namely, an input layer with a different number of neurons in the initial database.

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