Soft-sensing modeling of chemical oxygen demand in photo-electro-catalytic oxidation treatment of papermaking wastewater

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ABSTRACT

Photo-electro-catalytic (PEC) oxidation has been widely recognized as an effective technology for advanced treatment of papermaking wastewater. To optimize the oxidation process, it is important to monitor continuously the chemical oxygen demand (COD) of inflow and outflow wastewater. However, online COD sensors are expensive difficult to maintain, and therefore COD is usually analyzed off-line in laboratories in most cases. The objective of this study is to develop an inexpensive method for on-line COD measurement. The oxidation-reduction potential (ORP), pH, and dissolved oxygen (DO) of wastewater were selected as the key parameters, which consists of four different types of artificial neural network (ANNs) methods: multi-layer perceptron neural network (MLP), back propagation neural network (BPNN), radial basis neural network (RBNN) and generalized regression neural network (GRNN). These parameters were applied in the development of COD soft-sensing models. Six batches of papermaking wastewater with different pollution loads were treated with PEC technology over a period of 90 minutes, and a total of 546 data points was collected, including the on-line measurements of ORP, pH and DO, as well as off-line COD data. The 546 data points were divided into training set (410 data, 75% of total) and validation set (136 data, 25% of total). Four statistical criteria, namely, root mean square error (RMSE), mean absolute error (MAE), mean absolute relative error (MARE), and determination coefficient (R²) were used to assess the performance of the models developed with the training set of data. The comparison of results for the four ANN models for COD soft-sensing indicated that the RBNN model behaved most favorably, which possessed precise and predictable results with R²=0.913 for the validation set. Lastly, the proposed RBNN model was applied to a new batch of PEC oxidation of papermaking wastewater, and the results indicated that the model could be applied successfully for COD soft-sensing for the wastewater.

Keywords: COD; PEC oxidation; papermaking wastewater; soft-sensing.

1. INTRODUCTION

Pulp and paper industries generate a large amount of wastewater which contains a variety of pollutants possessing high amounts of chemical oxygen demand (COD). COD is an important parameter for real-time control and optimization in wastewater treatment. However, online monitoring and control of effluent COD is often impractical at paper mills, due to high cost of commercial on-line COD sensors. There is a need of inexpensive alternative methods for online COD monitoring.

Several methods with independent parameters have been reported for COD soft-sensing. Agarwal and Saxena proposed a basic statistical linear model calculates COD using several measured parameters; however, it fails to predict the COD accurately. Different nonlinear models were also proposed for COD prediction, such as principal component regression (PCR), partial least squares (PLS) regression, and artificial intelligence (AI) techniques. The models are effective in representing the correlations between input and output parameters in nonlinear complex systems, based on artificial neural networks (ANNs). For example, Yu et. al., utilized ANN models to predict the color of wastewater and the COD removal efficiency with the data of oxidation reduction potential (ORP), pH, and dissolved oxygen (DO) content of wastewater. In another case, Yilmaz et. al., developed a novel approach based on an ANN model to predict the effluent COD in an up-flow anaerobic filter (UAF) reactor.

In recent years, photo-electro-catalytic (PEC) oxidation has been regarded as having the highest potential for advanced oxidation processes (AOPs). We reported earlier a batch PEC oxidation process for advanced treatment of wastewater from paper mills. The PEC technology required higher precision and more responsive control for COD monitoring. With improvement in COD testing, the system has the potential to determine the endpoint of the degradation process to ensure that the effluents reach discharge standards. To determine COD on-line, soft-sensing methods were applied using three measurable parameters (ORP, pH and DO) in the PEC oxidation process of papermaking wastewater. Also, four COD prediction models were developed using ANN methods, which included a multi-layer perceptron (MLP) neural network, a back propagation neural network (BPNN), a radial basis neural network (RBNN), and a generalized regression neural network (GRNN). The performances of the four soft-sensing models were assessed...
using the sensitivity analyses. Finally, the best performing soft-sensing model was tested with wastewater samples from paper mills.

2. EXPERIMENTAL

An effluent sample from the sequential batch reactor (SBR) of activated sludge wastewater treatment was obtained from a secondary fiber paper mill in Guangzhou, China. It was treated further with the PEC technology in this study. The wastewater sample was pretreated by a flocculation process prior to the PEC oxidation process to remove suspended solid, as shown in Figure 1.

### 2.1 Flocculation stage

The pH value of the papermaking wastewater sample in a 2.0 L reactor was adjusted to 4 by adding 0.1 M HNO₃; 0.5 g of inorganic flocculant (polymeric ferric sulfate/poly aluminium chloride ratio of 3:2) and 0.06 g of nano-TiO₂ colloid (solids content of 35 wt%) were added to the reactor. The mixture was stirred at 500 rpm for 1 min, followed by 30 min of sedimentation. Then the sediments in the reactor were removed, and the upper clear water was used for the following PEC oxidation process.

### 2.2 PEC oxidation stage

The configuration of the PEC system, as shown in Figure 1, was composed of two photo-anodes that were aluminum-based honeycomb meshes with nano-TiO₂ on the surface. The photo-anodes were fixed at both sides of the UV lamps (30W). The counter electrode consisted of a sponge nickel on which hydrogen peroxide (H₂O₂) could be electrochemically reduced to DO. The reactor was equipped with an ORP probe (HAOSHI, China) with an Ag/AgCl electrode, a pH probe (ENTEX, Singapore), and a DO meter (CLEAN, USA) for on-line monitoring of the ORP/pH/DO parameters at every 1 min interval during the PEC oxidation process.

The PEC oxidation process was as follows. First, Nano-TiO₂ (3 g, solids content of 35 wt%) was added to the wastewater sample as the photocatalyst, H₂O₂ (4 ml, 35% v/v) as the oxidizing agent, and AC (aluminum-based honeycomb mesh) as the support material. After the PEC oxidation process, the treated effluent was collected and analyzed for COD, BOD, and other parameters.

**Figure 1.** Schematic diagram of the PEC oxidation reactor and data collection system

**Figure 2.** Advanced PEC treatment of 6 SBR effluents from paper mills with various COD loads
wt%) as the oxygen source, and Na$_2$SO$_4$ (1 g, AR) as the electrolyte for improving the PEC treatment efficiency. Then the mixture was mixed at 500 rpm and was treated with UV-irradiation. The PEC reaction time was 90 min, in which samples were taken at 1-min intervals for COD measurement according to the standard method. Six SBR effluent samples with COD loads varying between 200-400 mg/L were collected from the Guangzhou paper mill. Figure 2 shows the appearance of the 6 water samples before and after the PEC oxidation treatment.

2.3 Data pre-processing

546 sets of data were obtained from the PEC oxidation treatment of the six samples. The datasets were used for the development of COD soft-sensing models, of which 410 datasets (75%) were randomly selected for model training, and 136 datasets (25%) for validation. Prior to the development of the soft-sensing models, the COD data were filtered with a smoothing method, and moving average filters were used in this study. Scaling was also performed using Equation 1 below. All data was converted [-1, 1] range.

\[
x_k = \frac{(x_k - x_{\text{min}})}{(x_{\text{max}} - x_{\text{min}})}
\]

Where $x_{\text{max}}$ and $x_{\text{min}}$ are the maximum and minimum values of each column of data, respectively.

2.4 Modelling algorithms

ANNs are parallel computing systems similar to biological neural networks and consist of large numbers of processing elements that are interconnected. An ANN is a network of artificial neurons arranged in layers and connected to each other. The neurons nonlinearly transform the incoming signals with activation functions and distribute the results to other neurons. The input-output relationship is encoded in the connection weights that are adapted to minimize the errors between the network outputs and the targets.

In present study, four COD soft-sensing models were developed with ANN methods, which includes a multi-layer perceptron (MLP) neural network, back propagation neural network (BPNN), radial basis neural network (RBNN) and generalized regression neural network (GRNN). The theories of these four ANNs are summarized in subsequent sections and were developed with MATLAB R2012a (MathWorks, Inc).

2.5 Multi-layer perceptron (MLP) neural network

MLP neural networks are considered to be a powerful nonlinear black-box model for learning complex nonlinear relationships between the input and output variables. It consists of three layers: an input layer, a hidden layer, and an output layer. One of the most important parameters of the MLP network is its number of neurons in the hidden layer, and is usually determined by a trial-and-error algorithm. To investigate the performance of the model, the minimum square error (MSE) method was applied using Equation 2 below.

\[
\text{MSE} = \frac{1}{n} \sum_{i=1}^{n} (y_i - \hat{y}_i)^2
\]

Where $n$ is the number of training patterns, and $y_i$ and $\hat{y}_i$ are the observation and prediction values of the output, respectively.

Throughout MLP simulations, the adaptive learning rates were used for the purpose of faster system training speed and resolving local minima problems. Also used was the Levenberg-Marquardt algorithm for training the MLP neural networks, where each network was trained for 1000 iterations to get the optimal neural network models.

2.6 Back propagation neural network (BPNN)

Being a supervised learning technique, BPNN has recently been used to deal with the approximations of nonlinear maps. In general, an input layer, an output layer and one or more hidden layers are often included in the network. In this study, the network was trained at a learning rate of 0.01, a minimum error of 0.001 and an epoch size of 1000. It should be noted that the number of neurons in the hidden layer was of great importance for the performance of BPNN, and was determined by the trial-and-error method.

2.7 Radial basis neural network (RBNN)

RBNN is a type of feed forward neural network (FFNN), and it can approximate any arbitrary continuous functions with arbitrary precision. In this study, in order to achieve faster computation speeds and improved algorithm accuracy, the number of hidden layer neurons were equal to the numbers of samples in training set, and the weight values could be directly resolved by linear models. Since the performance of RBNN method depends on the spread coefficient, various spread coefficients were evaluated to achieve the optimal performance for the given problem.

2.8 Generalized regression neural network (GRNN)

A GRNN consists of four layers: an input layer, a pattern layer, a summation layer, and an output layer. The number of input units in the input layer depends on the total number of observation parameters. The first layer is fully connected to the pattern layer, where each unit represents a training pattern and its output is a measure of the distance of the input from the stored patterns. Each pattern layer unit is connected to the two neurons in the summation layer.

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3. RESULTS AND DISCUSSION

In the PEC oxidation treatment of the 6 wastewater samples of different pollution loads, 546 datasets were collected, which included measurements of COD, pH, ORP and DO of wastewater. These datasets were divided into two groups: training dataset (410 data sets) and validation dataset (136 datasets).

The procedure for the development of COD soft-sensing models with these datasets were as follows: (1) Data pre-processing; (2) Training and validation of soft-sensing models with their respective datasets; (3) Application of the model with new datasets.

3.1 Data pre-processing

In the data pre-processing stage, the moving average filter was implemented to smooth the off-line COD values with a common function in Matlab denoted as ‘smooth’. The moving average filters with a ‘span’ of 1-100 were applied and tested for the six samples undergoing PEC oxidation. As displayed in Figure 3, the filter with a ‘span’ of 20 exhibited favorable smoothing effects, and reflected the general tendencies of variation for COD during the PEC advanced treatment process.

3.2 Modeling results

Four COD soft-sensing models, MLP, BPNN, RBNN and GRNN, were developed with the ANN methods described in Section 2.4. For the purpose of comparison, four statistical indices were utilized: RMSE, MAE, MARE and $R^2$ which were calculated with following equations: performance was compared by means of RMSE, MAE, MARE and $R^2$ statistic parameters. As displayed in Table 1 above, the results of MLP, BPNN, RBNN and GRNN soft-sensing models in the training and validation phase were compared. It is recognized that small values of RMSE, MAE and MARE correlate to a high precision of the

\[
R^2 = 1 - \frac{\sum_{i=1}^{N} (Y_{measured,i} - Y_{predicted,i})^2}{\sum_{i=1}^{N} (Y_{measured,i} - \bar{Y})^2}
\]

\[
RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (Y_{measured,i} - Y_{predicted,i})^2}
\]

\[
MAE = \frac{1}{N} \sum_{i=1}^{N} |Y_{measured,i} - Y_{predicted,i}|
\]

\[
MARE = \frac{1}{N} \sum_{i=1}^{N} \left|\frac{Y_{measured,i} - Y_{predicted,i}}{Y_{measured,i}}\right| \times 100
\]
prediction models, and high $R^2$ value depicts close agreement between the datasets and the fitted model. These indicators represent favorable predictive behaviors for the model.

As seen in Table 1, the training phase showed poor performance for the MLP model, denoted by the low $R^2$ values. Although the MARE index of 13.678 (for the RBNN model) was low, the other indices (RMSE, and MAE) values for the RBNN model were low as well. This revealed that the RBNN model performed best when compared to the other four prediction models. Therefore, it could be summarized that in the training phase, the RBNN model is the preferred model of the four ANN models.

Table 1. Performance of the four soft-sensing models in the training and validation phases

<table>
<thead>
<tr>
<th>Models</th>
<th>Training phase</th>
<th>Validation phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RMSE (mg/L)</td>
<td>MAE (mg/L)</td>
</tr>
<tr>
<td>MLP</td>
<td>28.884</td>
<td>24.877</td>
</tr>
<tr>
<td>BPNN</td>
<td>20.583</td>
<td>12.973</td>
</tr>
<tr>
<td>RBNN</td>
<td>15.581</td>
<td>9.698</td>
</tr>
<tr>
<td>GRNN</td>
<td>17.156</td>
<td>10.522</td>
</tr>
</tbody>
</table>

Therefore, the RBNN model was chosen as the best model for estimating the COD values when using data from pH, ORP, and DO measurements of the wastewater in the PEC advanced treatment process.

3.3 Application of the RBNN soft-sensing model

Furthermore, the predicted COD values of the four models were compared with the measured values in the validation phase. As shown in Figure 4, the RBNN model demonstrated better performance than the other models, and was significantly superior to that of the MLP model. Also in Figure 4, the RBNN model showed strong correlations (high $R^2$ value) between the fitted model ($X=Y$) and the measured datasets. This indicates that the predictive ability for COD with the RBNN model is more effective when compared to the MLP, BPNN and GRNN models.

Figure 4. Validation phase and comparison results between the measured and predicted COD concentrations by MLP, BPNN, RBNN and GRNN models, respectively

(a) Variation of COD in the PEC advanced treatment process

To evaluate the applicability of the proposed RBNN soft-sensing model of COD, new wastewater samples were collected from the treatment plant of paper mill and subjected to the PEC advanced treatment process in the laboratory. During the PEC oxidation of the wastewater, on-line measurements of the ORP, pH, and DO of the process.
wastewater were applied to the RBNN model to predict the COD values and compared with the off-line COD measurements. The results are shown in Figure 5.

It can be seen from Figure 5(a) that the predicted COD values (points) correlate well with the measured values (line). Moreover, as shown in Figure 5(b), the scatter plot of the measured COD to predicted COD are in close agreement to the fitted line (X=Y), depicting effective predictive abilities for the RBNN model. For the model performance evaluation criteria, three points can be made: one, the MAE of COD was approximately 10 mg/L, which signifies that the error in prediction was in the range of acceptance; two, the R² was above 0.9, revealing that the predictive accuracy of the RBNN model was efficient, and the generalization ability was strong; and three, the MARE index within the test samples (11.645mg/L) was smaller than those in the training (13.678mg/L) and validation (14.351mg/L) phases, indicating that the error in predicting COD was comparatively low. From the analyses above, the proposed RBNN soft-sensing model has been demonstrated to be a reliable system for the prediction of COD in the PEC advanced treatment of papermaking wastewater.

4. CONCLUSIONS

In this work, four different artificial neural network (ANN) soft-sensing models, MLP, BPNN, RBNN and GRNN, were developed to predict the COD values of papermaking wastewater using the on-line data of pH, ORP, and DO in a lab-scale advanced PEC treatment process. In total, 546 datasets were collected and interpreted, wherein 410 of the datasets were used to train the models and the remaining 136 datasets for validating the developed models. The performance of the four models were compared and evaluated using four statistical indices: RMSE, MAE, MARE, and R². The results demonstrated that the RBNN model provided a more accurate prediction to the experimental COD, and obtained higher model performances indices (RMSE=16.136, MAE=10.259, MARE=14.351, and R²=0.913) than those of the MLP, BPNN and GRNN models. After the RBNN model was determined to be the best soft-sensing model, it was then applied to new testing wastewater samples undergoing PEC advanced treatment to assess the reliability and applicability of the proposed model. The results show that the proposed RBNN model demonstrated on-line COD predictability with acceptable accuracy, indicating its feasibility in the soft-sensing COD in PEC oxidation of papermaking wastewater.

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