On-line chemical oxygen demand estimation models for the photoelectrocatalytic oxidation advanced treatment of papermaking wastewater

Wenhao Shen, Feini Huang, Xuewen Zhang, Yuefei Zhu, Xiaoquan Chen and Nishonov Akbarjon

ABSTRACT

Chemical oxygen demand (COD), an important indicative measure of the amount of oxidizable pollutants in wastewater, is often analyzed off-line due to the expensive sensor required for on-line analysis. However, its off-line analysis is time-consuming. An on-line COD estimation method was developed with photoelectrocatalytic (PEC) technology. Based on the on-line data of the oxidation–reduction potential (ORP), dissolved oxygen (DO) and pH of wastewater, four different artificial neural network methods were applied to develop working models for COD estimation. Six different batches of sequence batch reactor (SBR) effluent from a paper mill were treated with PEC oxidation for 90 minutes, and 546 data points were collected from the on-line measurements of ORP, DO and pH, and the off-line COD analysis. After having training and validation with 75% and 25% of data, and evaluation with four statistical criteria (R², RMSE, MAE and MAPE), the estimation results indicated that the developed radial basis neural network (RBNN) model demonstrated the highest precision. Subsequently, the application of the RBNN model to a new batch of SBR effluent from the paper mill revealed that the RBNN model was acceptable for COD estimation during the PEC advanced treatment process of papermaking wastewater, which implied its possible application in the future.

Key words | ANN, COD, modeling, papermaking, PEC oxidation, wastewater

INTRODUCTION

The papermaking industry uses a large amount of water and generates wastewater that contains a variety of pollutants with high values of chemical oxygen demand (COD) (Lucas et al. 2012). Being one of the most important quality indexes of effluents, the COD value of wastewater is often used as a variable for real-time control and processing optimization. However, due to on-line COD sensors (photometric, UV and electrochemical methods) being expensive and the time delay of off-line measurement, effective monitoring and control of COD in effluents is often not a common practice in paper mills. Therefore, a new method using artificial neural networks (ANNs) to estimate the COD of papermaking wastewater on-line was developed in the study.

Some methods involving independent parameters have been reported for estimating COD. With limited prediction accuracy of the basic statistical linear model, a multiple analysis method calculating COD was developed (Nadiri et al. 2018). Some advanced methods, such as principal component regression, partial least squares regression (Kadlec et al. 2011) and artificial intelligence (AI) techniques (Maier & Dandy 2000; Banerjee et al. 2011; Nourani et al. 2012), have been proposed for estimating COD. Among these methods, the AI techniques were highly effective for presenting the correlations between the input and output parameters in nonlinear complex systems, where the methods based on ANN were the most popular (Yu et al. 2013). Yu et al. used ANN models to predict the color of wastewater and efficiencies of COD removal by monitoring the oxidation–reduction potential (ORP), dissolved oxygen (DO) and pH of wastewater (Yu et al. 2014). Yilmaz et al. developed an approach based on an ANN model to predict the COD in effluents from an up-flow anaerobic filter reactor (Yilmaz et al. 2010). These studies demonstrated the effectiveness of ANN models for the estimation of COD.
In recent years, the photoelectrocatalytic (PEC) oxidation process (Zainal et al. 2007; Xu et al. 2009) has been regarded as one of the advanced oxidation treatments of wastewater with the most potential. In previous studies, a batch PEC oxidation process was developed for the advanced treatment of papermaking wastewater (Wu 2015). In the batch process, to make the effluent COD meet the emission standard, it was necessary to monitor the COD during the PEC oxidation process. In the article, an approach to on-line estimation of COD in the PEC advanced treatment of papermaking wastewater was reported. Firstly four estimation models were developed with four different ANN methods that use three measurable parameters (ORP, DO and pH) of wastewater from the PEC oxidation process. Then comparisons of the four COD estimation models were made with their performance in terms of certain precision criteria. Finally, the identified best model was applied to a new batch of PEC treatment process for on-line estimation of COD in the wastewater released from a paper mill.

METHODS

The effluents of sequencing batch reactor (SBR) from the activated sludge process of wastewater treatment in Guangzhou paper mill were collected, and further treated by PEC advanced oxidation in a laboratory setup (Figure 1).

Flocculation treatment

Prior to the PEC treatment, a flocculation treatment was performed to remove the suspended solid in the wastewater. As showed in the left part of Figure 1, the flocculation was conducted as follows:

1. The pH value of the papermaking wastewater was adjusted to 4.0 by adding 0.1 M HNO₃.
2. 0.5 g of a ternary composite flocculant consisting of polymeric ferric sulfate/poly aluminum chloride (3:2, w/w) and 0.06 g nano-TiO₂ colloid (35 wt% dry mass) was added into the reactor.
3. After being stirred for 1 min, the aqueous mixture was allowed to settle for 30 min.
4. The supernatant was used for the PEC advanced oxidation treatment.

Photoelectrocatalytic advanced oxidation treatment

A laboratory-scale 2.0 L reactor for PEC oxidation equipped with a data acquisition system was constructed as illustrated in the right part of Figure 1. During the PEC oxidation process, 3 g nano-TiO₂ colloid (35 wt% dry mass, as the photocatalyst) and 4 mL H₂O₂ (35 wt%, as the oxidant) were applied to 2,000 mL wastewater. Na₂SO₄ (1 g, AR), a widely used electrolyte, was added to improve the PEC...
oxidation efficiency (Yao et al. 2012; Bessegato et al. 2015; Mumjitha & Raj 2015).

The reactor was operated under high-speed stirring at 600 rpm to degrade the organic substrate using PEC oxidation technology. With one UV lamp (30 W) on both sides, the photo anode was made of aluminum-based honeycomb mesh whose large specific surface area favoured the deposition of nano-TiO$_2$ on it. Sponge nickel was used as the counter electrode where the DO could be generated by the cathodic reduction of H$_2$O$_2$. A fixed bias voltage of 0.8 V was applied with a DC power supply (TASI, China). The PEC reactor was equipped with one ORP probe (HAOSHI, China) with an Ag/AgCl electrode, one DO meter (CLEAN, USA) and one pH probe (ENTEX, Singapore) to monitor the changes of ORP/DO/pH on-line during the PEC oxidation process. All the sensors were connected to a programmable logic controller (PLC; Siemens, Germany) that could communicate with the industrial personal computer (IPC). The software Kingview 6.53 (Wellintech, China) was used for the on-line data acquisition.

The whole PEC oxidation reaction was run for 90 minutes. The ORP, DO and pH values of the wastewater were recorded on-line every 1 min, and wastewater samples (2 mL each time) were simultaneously withdrawn for COD measurements off-line. The COD of the wastewater sample was measured by a digester (HACH, USA) and a spectrophotometer (HACH, USA) according to the standard method (issued by the Chinese Ministry of Environmental Protection 2008).

Experimental data for developing COD estimation models

In the current study, six batches of SBR effluent samples (as shown in Figure 2) with CODs varying from 200 to 400 mg/L,
covering almost the entire range of possible COD loadings, were collected and further treated with PEC oxidation technology. So a total of 546 data points, including the ORP, DO, and pH values acquired on-line and COD values obtained by off-line analysis, were applied to develop working models for on-line COD estimation.

Data pre-processing

Prior to the development of the working model for COD estimation, the necessary data pre-processing was applied to the acquired ORP, DO, pH, and COD data.

Normalizations were conducted with the on-line data of ORP, DO and pH by Equation (1).

\[ x'_{k} = \frac{x_{k} - x_{\text{min}}}{x_{\text{max}} - x_{\text{min}}} \]  

where \(x_{k}\) and \(x'_{k}\) were the data values before and after normalization; \(x_{\text{max}}\) and \(x_{\text{min}}\) were the maximum and minimum values of each type of measurement, respectively.

Experimental data errors could be caused by the manual samplings of wastewater during the PEC oxidation process and by actual measuring errors of COD. So a moving average data filter was applied to smooth the off-line COD data:

\[ y_{f}(k) = \frac{y(k) + y(k-1) + y(k-2) + \ldots + y(k-N+1)}{M} \]  

where \(y(k)\) and \(y_{f}(k)\) were the COD values before and after filtering, respectively; \(k\) was the sampling time, and \(M\) was the time range of the moving average data filter.

Modeling algorithms

ANNs are parallel computing systems similar to biological neural networks and consist of large numbers of processing elements with interconnections (Yilmaz et al. 2010). The neurons nonlinearly transform the input 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 (Haimi et al. 2013).

In this study, four working models for COD estimation were developed with different ANN methods, including multi-layer perceptron neural network (MLP), back propagation neural network (BPNN), radial basis neural network (RBNN) and generalized regression neural network (GRNN). All of the ANN models were developed with MATLAB, which has been recognized as the professional software to develop different algorithms with data. Their principles are described concisely as follows.

Multi-layer perceptron neural network

MLP neural network is considered to be powerful nonlinear model for learning complex nonlinear relationship between the input and output variables (Abbasi & Eslamloueyan 2014). It consists of three layers: input layer, hidden layer and output layer. One of the most important parameters of the MLP neural network is the number of neurons in the hidden layer, which is usually determined by the trial-and-error method.

During the MLP modeling, adaptive learning rates were used for the purposes of faster training speed and solving local minimal problems. In this study, the Levenberg-Marquardt algorithm was used for training the MLP neural networks, and each network was trained 1,000 times to get the optimal neural network models.

Back propagation neural network

As a supervised learning technique (Zhang et al. 2013), BPNN has recently been used to deal with the approximations of nonlinear problems. In general, one input layer, one output layer and one or more hidden layers are included in the network. In this study, the network was trained at the learning rate of 0.01, minimum error of 0.001 and epoch size of 1,000. It should also be noted that the number of neurons in the hidden layer was of great importance for the performance of the BPNN, and it was determined by the trial-and-error method based on the empirical equation.

Radial basis neural network

RBNN is a feed forward neural network and can approximate any arbitrary continuous functions with arbitrary precision (Montazer et al. 2013). In the study, to achieve fast computation speed and improve algorithm accuracy, the numbers of hidden layer neurons were equal to the numbers of samples in the training set (Shi et al. 2011), and the values of weights could be directly solved by linear equations. Since the performance of the RBNN method depends on the spread coefficient, different spread
coefficients were tried, to achieve the optimal performance for the given problem.

Generalized regression neural network

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

Model evaluation index

As in the above descriptions, four different programs were coded for the developments of the MLP, BPNN, RBNN and GRNN working models for COD estimation. In general, the number of neurons in the hidden layer is one of the key elements to develop an ANN model: too many or too few elements to develop an ANN model: too many or too few

\[ \text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (Y_i^{\text{measured}} - Y_i^{\text{estimated}})^2} \]  

\[ \text{MAE} = \frac{1}{N} \sum_{i=1}^{N} |Y_i^{\text{measured}} - Y_i^{\text{estimated}}| \]  

\[ \text{MAPE} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{Y_i^{\text{measured}} - Y_i^{\text{estimated}}}{Y_i^{\text{measured}}} \right| \times 100\% \]

where \( N \) denotes the number of observations, \( Y \) is the COD value.

RESULTS AND DISCUSSION

Selection of secondary variables

The selection of secondary variables plays an important role in estimation modeling. Based on the mechanism of PEC oxidation technology, the variables of ORP, DO and pH of wastewater were strongly related to the COD value (Wu 2015), and their evolutions observed during the PEC oxidation process are shown in Figure 3 and could be explained as follows:

(1) Being a variable measured conveniently at affordable cost, ORP has been widely applied for monitoring wastewater treatment and chemical oxidation processes (Song 2012; Yu 2004; Zanetti et al. 2012). It has been proved that the hydroxyl radical, a strong oxidant generated in the PEC oxidation process, could significantly enhance the redox potential of PEC, leading to the degradation of organic contaminants in wastewater (Daghrir et al. 2012; Shukla & Madras 2014).

(2) The DO value of wastewater could reflect the relative amount of \( \text{H}_2\text{O}_2 \) consumed in the oxidation-reduction reactions (Daghrir et al. 2013). Firstly, as per the PEC advanced oxidation treatment process shown in Figure 1, in the early stages of PEC, the effect of the applied bias voltage predominates, which results in a high DO concentration due to the electrooxidation of the \( \text{H}_2\text{O} \) molecule at the anode (Chang et al. 2009; Daghrir et al. 2012). However, in the later part of the PEC process, under the irradiation of the ultraviolet lamps, the concentration of DO declines, since the oxygen is consumed to form the superoxide radicals \( \text{O}_2^- \) and subsequently the other oxidant species such as \( \text{H}_2\text{O}_2 \), \( \text{H}_2\text{O}^- \) and \( \text{HO}_2^- \) (Daghrir et al. 2012), which can be explained by the band theory. The recombination of the holes on the valence band (hVB +) and the electrons on the conduction band (eCB) of \( \text{TiO}_2 \) have been regarded as an inhibiting process in photocatalysis. Acting as a scavenger for the photon-induced electrons on the conduction band of the \( \text{TiO}_2 \) surface, the dissolved \( \text{O}_2 \) in the wastewater delays the recombination of the electron hole and becomes a peroxide radical (Ugurlu & Karaoglu 2009).

(3) In the PEC oxidation process, \( \text{H}^+ \) could be generated and consumed continuously, which leads to the decline
and rise of the pH values during the PEC oxidation treatment.

According to the above discussion, the ORP, DO and pH of wastewater were chosen as the secondary variables to develop working models for COD estimation in the PEC oxidation process.

Data pre-processing

As described in this work, 546 data points, including the ORP, DO, and pH on-line values as well as COD values measured off-line, were collected from the PEC advanced oxidation of six batches of SBR effluent samples. Subsequently, these data were divided into two groups randomly, i.e. the training set (75%, 410) and the validation set (25%, 136), which were used for the developments of the COD estimation models.

The steps for developing the working models for COD estimation were as follows: (1) Data pre-processing; (2) Developing the working models with training and validation of the data points, in that order; (3) Applying the working model to a new batch of wastewater.

Before the model development, as described above, the on-line measured data of ORP, DO and pH were normalized according to Equation (1) and the COD data obtained off-line were pre-processed with the moving average filter according to Equation (2). After the COD filtering pre-processing, as plotted in Figure 4, except for the RMSE of RBNN model and the R² for GRNN model, the performance criteria (R², RMSE, MAE and MAPE) of four working models were generally improved, which suggested the necessity of the COD filtering pre-processing. Among the four estimation models, the BPNN model showed the best filtering effect and its MAPE criterion was improved by 16%; its other three evaluation criteria (R², RMSE and MAE) were also improved.

Development of working models for estimating COD

Four working models were developed using various ANNs including MLP, BPNN, RBNN and GRNN. With the
trial-and-error method for training these models, the optimal key parameters were obtained and listed in Table 1, and the MSEs of various working models are illustrated in Figure 5.

With the data of the training set and the optimal key parameters in Table 1, four COD working models were developed with different ANN methods, i.e. MLP, BPNN, RBNN and GRNN. Their criteria in the training phase were compared in Table 2.

It is well recognized that small values of RMSE, MAE and MAPE indicate the high precision of estimation models, and that the value of $R^2$ should be close to 1 as far as possible, which represents an excellent estimation result. Following this principle, in the training stage, the performance of the MLP model was the worst. Although the MAPE value of 13.7 for the RBNN model was not the lowest, the RMSE and MAE of the RBNN model were the lowest and the $R^2$ for RBNN model was the highest, suggesting that the RBNN model was the best among these models.

Subsequently, the four ANN working models for COD estimation were validated using the validation data set. Clearly, as displayed in Table 2, the validation results for RBNN were similar to or even better than those obtained in the training stage, confirming its optimal performance.

In addition, the measured and estimated CODs from the four models in the validation stage were compared. As shown in Figure 6(c), it is evident that the all data points from the RBNN model are located closer to the bisector than those from the other three models, indicating that the RBNN model was the best for estimating COD.

The above results from the training and validation phases suggested that the RBNN model developed was the

Table 1 | The optimal key parameters in the training of four estimation models

<table>
<thead>
<tr>
<th>Estimation models</th>
<th>MLP</th>
<th>BPNN</th>
<th>RBNN</th>
<th>GRNN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of neurons in the hidden layer</td>
<td>18</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Spread coefficient</td>
<td>–</td>
<td>4.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 2 | Performance of working models for COD estimation

<table>
<thead>
<tr>
<th>Models</th>
<th>Training phase/validation phase</th>
<th>$R^2$</th>
<th>RMSE (mg/L)</th>
<th>MAE (mg/L)</th>
<th>MAPE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLP</td>
<td>0.672/0.645</td>
<td>28.9/29.6</td>
<td>24.9/26.7</td>
<td>40.8/49.9</td>
<td></td>
</tr>
<tr>
<td>BPNN</td>
<td>0.885/0.874</td>
<td>20.6/21.1</td>
<td>13.0/13.1</td>
<td>18.5/20.0</td>
<td></td>
</tr>
<tr>
<td>RBNN</td>
<td>0.920/0.913</td>
<td>15.6/16.1</td>
<td>9.70/10.2</td>
<td>13.7/14.4</td>
<td></td>
</tr>
<tr>
<td>GRNN</td>
<td>0.889/0.868</td>
<td>17.2/18.0</td>
<td>10.5/11.8</td>
<td>13.0/16.9</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5 | Influences of the key parameters of four working models on MSE.
best one for estimating COD based on the ORP, DO and pH values of wastewater in the PEC advanced oxidation process.

Compared with other work using ANN methods for estimating the COD of wastewater based on data, some different results have been obtained. In a upflow anaerobic filter (UAF) reactor treating wastewater containing cyanide, the COD and other two parameters in the influent were used to estimate the effluent COD with different ANN methods, and the result showed that the MLP model was found to be better than the RBNN and GRNN models, and the R² for the MLP model was 0.876, which was lower than that of the RBNN model in the present study (Yilmaz et al. 2010). One feedforward BPNN model was developed to predict the COD in an aerobic granulation process; the obtained R² of the prediction model was only 0.490, which was much lower than the R² = 0.911 in the present study (Gong et al. 2018). These comparisons reveal that, although ANN methods have been applied in different wastewater treatment processes and their effectiveness has been demonstrated, conducting PEC advanced treatment even with the wastewater sampled from the paper mill in this study led to a high COD estimation accuracy with the developed RBNN model.

Application of the COD estimation model

To test the applicability of the proposed RBNN model for estimating COD, a new batch of SBR effluent was collected from the same paper mill and treated by PEC advanced oxidation in our laboratory. During the PEC oxidation process, the on-line data of ORP, DO and pH of wastewater were acquired and applied to the developed RBNN model, and the COD values were estimated by the RBNN model and compared with the actual off-line CODs (Figure 7).

In Figure 7(a), it can be seen that the estimated CODs (solid line) are close to the measured CODs (dotted line). Moreover, when presented as shown in Figure 7(b), the scatter of the measured-estimated CODs is close to the bisector, indicating that the developed RBNN model was the best one for estimating COD.

Using the developed RBNN model with the testing batch of wastewater, the RMSE and MAE of CODs were |

Figure 6 | Correlations of the measured and estimated CODs with four models in the validation phase.
15.136 mg/L and 10.332 mg/L, respectively, suggesting that the estimated CODs accuracy were acceptable. The MAPE of CODs for the testing batch was 11.645%, which was even smaller than those (13.678% or 14.351%) obtained in the training or validation stage (Table 2), indicating a comparatively low estimation error from the RBNN model. The obtained $R^2$ of 0.921 revealed the good correlation between the off-line measured COD values and those estimated by the RBNN model.

**CONCLUSIONS**

Using ANNs and taking the on-line acquired ORP, DO and pH values as the input variables, one solution to on-line estimation of COD in wastewater during the PEC advanced oxidation treatment process was put forward. Based on 546 data points acquired from six batches of the PEC process, the performances of four ANN models were evaluated and compared in terms of four criteria: $R^2$, RMSE, MAE and MAPE. Of the four ANN models (MLP, BPNN, GRNN and RBNN), the RBNN model performed best according to the training (with 410 data points) and validation (with 146 data points) results. The developed RBNN model was further applied to another testing batch of the PEC advanced oxidation process with the wastewater that was randomly. The calculated RMSE, MAE, MAPE and $R^2$ from the RBNN model for the testing batch were 15.136 mg/L, 10.332 mg/L, 11.645% and 0.921, respectively. Such results suggested that, using the on-line measured data of ORP, DO and pH, the developed RBNN model could be used to estimate CODs on-line with acceptable accuracy, which showed the great potential for application in COD estimation during the PEC advanced treatment of papermaking wastewater in a pilot system.

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**REFERENCES**


Nourani, V., Baghanam, A. H. & Gebremichael, M. 2012 Investigating the ability of artificial neural network (ANN) models to estimate missing rain-gauge data. *Journal Environmental Informatics* 19 (1), 38–50.


