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ANN prediction of decolourisation efficiency of organic dyes in wastewater by plasma needle

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Abstract: In this paper, the results of decolourisation of Reactive Orange 16 (RO 16), Reactive Blue 19 (RB 19) and Direct Red 28 (DR 28) textile dyes in aqueous solution by plasma needle are presented. Treatment time, feed gas flow rate (1, 4, 8 dm³/min) and gas composition (Ar, Ar/O₂) were optimized to achieve the best performance of the plasma treatment. Artificial Neural Network (ANN) was used for the prediction of parameters relevant for the decolourisation outcome. It was found that more than 95 % decolourisation could be achieved for all three dyes after plasma treatment, although the decolourisation of DR 28 was much slower than the other two dyes, and this could be explained by the complexity of its molecular structure. It was concluded that oxidation was very depended on all three mentioned parameters. ANN predicted the treatment time as the crucial factor for decolourisation performance of RO 16 and DR 28, while Ar flow rate was the most relevant for RB 19 decolourisation. The obtained results suggest that the plasma needle is a promising tool for oxidation of organic pollutants and that ANN can be used for optimization of treatment parameters to achieve high removal rates.

Keywords: textile dyes, oxidation, plasma discharge.

INTRODUCTION

Hazardous effects of increasing industrialization and agriculture affect water ecosystem and human health directly. Considering amounts of various industrial wastewaters are discharged into different water bodies thus influencing the activities in the water purification research area. Due to their operations, the textile, food and paper industries generate very complex and diverse effluents and they are rated as one of the most polluting among all industrial sectors.¹ The main components of these effluents are organic dyes (colourants), noted in the literature as very toxic, mutagenic and carcinogenic.²–⁴ About 700 000 tons of textile
Dyes produced annually are discharged into different water bodies disturbing their quality directly (colour, chemical oxygen demand (COD), biological oxygen demand (BOD), suspended solids, temperature, pH, dissolved O₂, etc.).

Among all categories widely used in industry, there are azo and anthra-quinonic types of dyes. Since they are made to be very chemically resistant and stable, mineralization by bacterial activity is very low and the water purification treatment very demanding. Some of the traditional techniques such as biological treatment, adsorption, nanofiltration, ozonation are being already used but with some limitations. The biggest problem concerning all mentioned processes is forming secondary pollution with no complete degradation of the final disposal.

Hence, very strict international environmental standards must be accomplished. In order to achieve these restrictions (ISO 14001, Directive 2000/60/EC of the European Parliament - WFD), many conventional technologies have been used for effective decolourisation and degradation of various pollutants as we have seen, but due to their inefficiency, operational and economical expenses, other alternative approaches had to be studied.

During the last few decades, Advanced Oxidation Processes (AOPs) have attracted big attention for water purification treatment as very suitable for the degradation of colourants which are resistant to above mentioned common technologies. They are used successfully in mineralization of soluble complex organic pollutants up to CO₂, H₂O and inorganic ions without any additional waste treatment and disposal. Compared to common chemical oxidizing processes such as chlorination and ozonation, they don’t produce any toxic byproducts.

Among all AOPs (UV/H₂O₂, UV/ultrasound, photo-Fenton, heterogeneous photocatalysis UV/TiO₂ etc.) plasma processes have also been investigated as a novel method for wastewater decontamination. There are various types of non-thermal plasma devices such as plasma jets, plasma needle, gliding arc, etc. These methods have the strong oxidizing ability and include simple operating conditions such as temperature and atmospheric pressure. Producing electrons, radicals (hydroxyl radical - OH⁺, hydrogen radical - H⁺, hydroperoxy radicals - HO₂⁺), Ions (OH⁻, H₂O⁺, H⁺, HO₂⁻) and neutrals (H₂O₂, O₃) with very high reduction potentials, powerful UV radiation and shock waves, plasma decomposes organic matter with no additional procedures and no sludge production. These characteristics make it convenient for different applications: sterilization, decontamination, purification, etc.

Plasma oxidation processes in liquids have been widely examined. Through the plasma treatment, various complex chemical reactions are initiated in the solution which is being treated. It is concluded that the oxidation mechanisms take place because of the formation of reactive radicals which strongly depend on the quality and quantity of the feed gas and treated sample properties.
ANN is a powerful technique for modelling nonlinear multivariable systems, where variables may have complex interrelationships that cannot be easily defined, like in plasma oxidation processes. Concerning the complexity of the oxidation mechanism initiated by the AOPs, the modelling of the removal process using artificial neural network (ANN) techniques is previously investigated as it does not require the mathematical description of the observed process. In the current study, ANNs are applied for the prediction of decolourisation efficiency of organic dyes by plasma discharge treatment by changing the process conditions.

The main goal of this work was to estimate the efficiency of the plasma oxidation process on the various textile dyes samples by finding the best operational parameters (treatment time, flow rate and composition of the feed gas) and the possibility of prediction the oxidation effects based on the ANN algorithms.

EXPERIMENTAL

All dyes were Sigma–Aldrich (St. Louis, MO, USA) and used without any further purification. Their main characteristics are given in Table I while structural formulas are presented in Fig. 1.

### TABLE I. Main characteristics of the model dyes used in plasma treatment

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Functional group</th>
<th>C. I. name</th>
<th>Molecular weight, g/mol</th>
<th>Wavelength (max), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reactive Orange V-3R</td>
<td>Reactive Blue 19</td>
<td>Direct Red 28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Azo</td>
<td>Anthraquinone</td>
<td>Azo</td>
<td></td>
</tr>
<tr>
<td>Reactive Orange 16 (RO 16)</td>
<td>617.54</td>
<td>626.54</td>
<td>696.66</td>
<td></td>
</tr>
<tr>
<td>Reactive Blue 19 (RB 19)</td>
<td>493</td>
<td>592</td>
<td>497</td>
<td></td>
</tr>
</tbody>
</table>

Fig 1. Structural formulas of textile dyes used in plasma treatment:

a) RO 16, b) RB 19, c) DR 28

Dye samples were prepared with distilled water (c = 50 mg/l, V = 50 ml). Plasma needle setup used in this research (Fig. 2) comprised of a Teflon body with the copper electrode
placed in the glass cylinder. Detailed characterisation of this plasma source is presented elsewhere. The needle tip was immersed in the solution. Magnetic stirrer (300 rpm) preserved the homogeneity of the sample. We used different Ar flow rates (1, 4, and 8 dm³/min) and different percentage of added O₂ in the feed gas. Plasma oxidation effect was determined by measuring the decolourisation rate of the dyes. After all treatments, the samples were analysed with UV/VIS (Varian Superscan 3, USA) by measuring absorbance (A) at characteristic wavelengths (Table I).

![Fig. 2. Plasma needle experimental setup](image)

The ANN architecture used in this study is consisted of several layers of neurons, namely the input layer, the hidden layer(s) and the output layer (Fig. 3). The ANN works by introducing the values of available inputs to the neurons of the first layer, where each input value is multiplied by a coefficient (weight) and forwarded to the neurons in the hidden layer in which the weighted sum is computed. Finally, the results are then forwarded to the output layer and compared to the measured values in order to evaluate model performance.

![Fig. 3. Graphic representation of the created ANN model](image)

Among various ANN algorithms, the general regression neural network (GRNN) demonstrated very good results in fitting complex systems with a limited set of training data. In present work, this architecture is selected because of its ability to fit multidimensional datasets even with sparse data points. The GRNN structure is fully adjusted
to the modelling system, namely the size of each of four layers (expressed as the number of neurons) depends only on the number of used input/output variables and data patterns in the dataset used for training.

The training process between the input layer and the hidden layer is composed of unsupervised learning, while the training between the hidden layer and the summation layer is composed of supervised learning, with the aim to minimize the difference e.g. the mean square error, between the model output and target value. More details on GRNN algorithm can be found in relevant literature.

RESULTS AND DISCUSSION

Plasma oxidation process

During the plasma treatment, many chemical reactions are introduced as a consequence of inelastic collisions of high-energy electrons coming from the plasma with water molecules (Fig. 4)

\[ \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2\text{O}^* + \text{e}^- \] (1)

According to literature, these collisions lead to the most significant processes such as vibrational or rotational excitation of neutral water molecules (Eq. 1):

\[ \text{H}_2\text{O}^* + \text{H}_2\text{O} \rightarrow \text{OH}^* + \text{H}^* + \text{H}_2\text{O} \] (2)
\[ \text{H}_2\text{O}^* + \text{H}_2\text{O} \rightarrow \text{O} + \text{H}_2 + \text{H}_2\text{O} \] (3)
\[ \text{H}_2\text{O}^* + \text{H}_2\text{O} \rightarrow \text{O} + 2\text{H}^* + \text{H}_2\text{O} \] (4)

If the electron energy is high enough to overcome the water dissociation threshold (\(>7\ \text{eV}\)) then other reactions can occur, leading to the water molecule dissociation (Eq. 5):

\[ \text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^* + \text{H}^* + \text{e}^- \] (5)
Production of radicals by plasma discharge in water has been examined by optical emission spectroscopy. It has been reported that the key radical species in plasma are very powerful oxidizing species \( \text{OH}^* \) formed as a consequence of vibrational/rotational excitation of water (Eq. 2) or directly by the electron impact dissociation of water (Eq. 5).\(^{20}\) Having the standard reduction potential of \( E^0 = 2.85 \text{ V} \) it can initiate the decolourisation reactions by reacting with the dye molecules with a high reaction rate (\( \approx 10^9 \text{ L mol}^{-1} \text{ s}^{-1} \)).\(^{29}\)

Chemical properties (possibility of oxidation, biodegradation) of the dyes are related to the chemical structure of each dye. Three textile dyes were chosen as representatives because of their different structures. RO 16 and DR 28 are categorized as azo dyes where RO 16 has one azo group (\( -\text{N}=\text{N} - \)) and DR 28 two as chromophores. RB 19 with chromophore groups \( =\text{C}=\text{O} \) and \( =\text{C}=:\) forming an anthraquinone complex was selected as a representative from the class of anthraquinones. All three dyes are characterized by high chemical stability and resistance to conventional physical and chemical degradation processes due to their complex, aromatic composition.\(^{29,30}\)

The oxidation rate of dyes was determined following the colour loss (decolourisation) process. It was the evidence that the chromophore group which was responsible for the absorption of the dye molecule in the visible region of the spectral range had been eliminated. Decolourisation rates for all three colourants are presented in Figs. 5 and 6.

The most noticeable fact is that the decolourisation was faster at the beginning of the plasma treatment and slowed down as the treatment continued as a consequence of different affinity of the reactive species for the different parts of the dye molecule. Radicals initially attacked the chromophore group, causing simultaneously fast decolourisation. Subsequently, benzene and naphthalene group of the dye molecules were probably mineralized until lower molecular weight acids and \( \text{CO}_2 \), amino groups until nitrate, azo groups until gaseous \( \text{N}_2 \) and sulfonates until sulphates.\(^{31,32}\)

Fig. 5 reveals an absorbance decrease and almost total decolourisation achievement after a certain time of plasma treatment (depending on the dye) for all Ar flow rates (1, 4 and 8 \( \text{dm}^3/\text{min} \)). RO 16 and RB 19 have similar decolourisation trend while DR 28 is found to be much more demanding for complete decolourisation. A faster decolourisation rate is evident as the Ar flow rate increases. Comparing the decolourisation kinetics for 1, 4 and 8 \( \text{dm}^3/\text{min} \) during the first 30 min of treatment the decolourisation rate significantly increases especially for the RO 16 and RB 19. However, after 30 min, the increase of flow rate does not contribute that much to the decolourisation rate. Namely, for only 15 min of RO 16 treatment, 80 % of dye was decolourised (8 \( \text{dm}^3/\text{min} \)), 60 % for 4 \( \text{dm}^3/\text{min} \) and only 30 % for 1 \( \text{dm}^3/\text{min} \). RB 19 did not follow this pattern.
The difference between 1 and 4 dm$^3$/min is obvious indicating that the feed gas flow rate is crucial for the oxidation process reducing the time for complete decolourisation from 120 to 60 min. Regarding the DR 28, having in mind the complexity of its molecular structure, it was very demanding to achieve satisfying decolourisation effect, but we succeeded with prolonged treatment time. It is evident that the time for entire decolourisation is prolonged than for two previous dyes and that the feed gas flow rate also did not have a satisfying influence on the oxidation effect as for RO 16 and RB 19.

Accordingly, the decolourisation rates followed order: RO 16 $>$ RB 19 $>$ DR 28. This order was caused by the diverse molecular structure of each dye. Anthraquinone dyes (RB 19) are more resistant to degradation due to their fused aromatic structures which are stabilized by resonance compared to azo ones (RO 16). The results obtained in this research are in agreement with studied literature where it is confirmed the faster RO 16 decolourisation process with ozone.
oxidation compared to RB 19. The smallest decolourisation rate of DR 28 can be explained by the large aromatic molecule with two conjugated azo groups (chromophores) which intensify the colour of the dye leading to the prolonged time of oxidation process.

Though, when we added a certain percentage (2 or 5 %) of O₂ in the feed gas (Fig. 6) for the same flow rate (4 dm³/min), the decolourisation performance was significantly enhanced especially for RB 19.

Namely, the time for the total oxidation was shortened from 60 to 15 min (2 %) and even faster decolourisation was accomplished (5 min) by increasing the O₂ amount (5 %) in the feed gas. The similar trend is observed for RO 16. The required time for total decolourisation outcome was reduced from 60 to 45 min but the difference between 2 and 5 % of O₂ didn’t influence the decolourisation rate degree as for RB 19. Fig. 6 also reveals the fact that the DR 28 was again the most problematic to decolourise even with the O₂ included (2 and 5 %). The time for the final oxidation result was evidently shorter, but still very long, and the increase of the O₂ amount in the feed gas was proposed to 10 %. However, the satisfactory results weren’t attained because the treatment time was still very long (150 min).

According to the Gumuchian et al. the better oxidation rates of all dyes can be attributed to the higher concentration of excited hydroxyl radicals in the mixture of Ar and O₂ as feed gas than for pure Ar. Besides this, with introducing the O₂ in the feed gas the generation of O and O₃ as the leading oxygen-based active species is enlarged. When O₂ is in contact to an electrical discharge, O atom (E₀ = 2.42 V) can be generated via dissociation of O₂ (Eq. 6) and directly react with contaminants or it can improve the OH• production (Eq. 7). 35–37

\[
\text{O}_2 + e^- \rightarrow 2\text{O} + e^- \quad (6)
\]

\[
\text{O}^\bullet + \text{H}_2\text{O} \rightarrow 2\text{OH}^* \quad (7)
\]

\[
\text{O} + \text{O}_2 + \text{M} \text{ (third body)} \rightarrow \text{O}_3 + \text{M} \quad (8)
\]

Additionally, O atom can also take part in the reactions with O₂ resulting the formation of O₃ (E₀ = 2.07 V) which has relatively high half-life of about 15 min (Eq. 8) and rapidly destructs the conjugated chains of the dye molecules (responsible for the colour intensity) leading to the fast oxidation with rate constants in the range of 10⁴ and 10⁷ L / (mol s). 10

Therefore, various active species are generated in different operating conditions and it could explain the difference between the decolourisation rates for all dyes. In the case with the pure Ar, OH• is the dominant reactant 35 but with O₂ included a large amount of oxygen-based species are formed leading to the better decolourisation efficiency. It is consistent with Jiang et al. who have previously demonstrated that the plasma oxidation treatment was the best with O₂ as the feed gas followed by air and Ar, and the least for nitrogen. 36
Fig. 6. Decolourisation rates of textile dyes: a) RO 16, b) RB 19 and c) DR 28 during plasma treatment for different composition (■ 2% O₂, ● 5% O₂, ▲ 10% O₂) of feed gas (4 dm³/min)

Therefore, various active species are generated in different operating conditions and it could explain the difference between the decolourization rates for all dyes. In the case with the pure Ar, OH⁻ is the dominant reactant but with O₂ included a large amount of oxygen-based species are formed leading to the better decolourisation efficiency. It is consistent with Jiang et al. who have previously demonstrated that the plasma oxidation treatment was the best with O₂ as the feed gas followed by air and Ar, and the least for nitrogen.

GRNN development and results

The input layer of the GRNN used in this study consisted of 3 neurons (one for each input variable), the pattern layer had one neuron for each pattern (Table SI Supplementary Material), the summation layer was composed of two neurons (one for the only output variable plus one), and the output layer had one neuron for the output variable (Fig. 3). After the architecture parameters were set,
GRNN was trained using genetic adaptive module provided by Neuroshell2.\textsuperscript{38} It uses genetic algorithm to find the optimal values of individual smoothing factors (ISFs) for each input as well as an overall smoothing factor (SF). The SF determines the GRNN accuracy, while the ISFs can be used for sensitivity analysis since their values indicate the input’s significance, \textit{i.e.} the input with larger ISF value is more important to the model.\textsuperscript{39}

Available data for each dye was random split into three datasets, namely training dataset for weights adjustment, validation dataset for smoothing factor determination, and test dataset for GRNN generalization performance assessment, in the ratio 65:70:20:10-15, respectively, depending on initial size of available data. Descriptive statistics for each dataset is presented in Table SIIa,b,c (Supplementary Material). The performance of each GRNN model is described by common performance metrics in Fig. 7 and Table SI (Supplementary material).

![Fig. 7. Measured and predicted absorbances (by GRNN) of decolourisation process for textile dyes: a) RO 16, b) RB 19 and c) DR 28](image)
Low values of RMSE and MAE, as well as high values of $R^2$ ($R^2 > 0.95$), indicated that data was fitted very well by GRNN models. Furthermore, sensitivity analysis performed using obtained ISF values (Table II) confirms that the significance of each input was well captured by created models. Namely, Table II also reveals that the most dominant factor for plasma decolourisation process of RO 16 and DR 28 generally was treatment time.

**TABLE II.** Evaluation of the GRNN sensitivity analysis based on the ISF values for inputs used in created models

<table>
<thead>
<tr>
<th>Name</th>
<th>RO 16</th>
<th>RB 19</th>
<th>DR 28</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$ / min</td>
<td>2.64</td>
<td>2.11</td>
<td>2.76</td>
</tr>
<tr>
<td>$Q$ / dm$^3$ min$^{-1}$</td>
<td>0.74</td>
<td>2.25</td>
<td>1.56</td>
</tr>
<tr>
<td>$O_2$ content, %</td>
<td>0.66</td>
<td>0.91</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Significance of flow rate and composition of the feed gas were dependent on the specific dye. In the case of RO 16, the flow rate and amount of the $O_2$ contributed oxidation effectiveness almost equally, unlike the DR 28 where the amount of $O_2$ was the least important. The influence of the $O_2$ was most perceptible for the RB 19 treatment which decolourised much faster than pure Ar for the same flow rate. Still, two crucial parameters (of the same importance) for RB 19 oxidation process were the treatment time and Ar flow rate.

**CONCLUSIONS**

In this article, we represent the plasma needle as an effective technology for decolourisation of the various organic dyes (RO 16, RB 19 and DR 28). The decolourisation effects were correlated to the different molecular structures of the tested azo and anthraquinone dyes, duration of the treatment, quality and quantity of the feed gas. We established that treatment time, Ar flow rate and $O_2$ content in the feed gas had a different effect on the decolourisation rate for each colour. The increase of the Ar flow rate and $O_2$ content generally improved oxidation rate but depending on the dye molecule it was more or less noticeable. Due to its molecular structure azo dye, DR 28 exhibited the smallest decolourisation rate than for RO 16 and RB 19 even with the increase of Ar flow rate and $O_2$. RB 19 was easier to decolourise than DR 28, but the $O_2$ introduction in the feed gas remarkably influenced its oxidation degree reducing the time for total colour loss from 90 to 15 min (5 % $O_2$). The RO 16 achieved the highest oxidation rate and changing feed gas conditions showed even better oxidation performances.

According to the ANN models, decolourisation efficiency can be predicted with satisfactory accuracy ($R^2 > 0.95$). These models also suggest that the duration of the plasma oxidation process was the most influential factor for the decolourisation effectiveness for RO 16 and DR 28. However, the feed gas flow rate and composition were very significant for RB 19 oxidation unlike the RO 16
where both parameters had the same (smaller) effect on the oxidation result. Ar flow rate manifested higher contribution degree to the DR 28 oxidation process than the amount of O\textsubscript{2} in the feed gas. Further investigations will optimize oxidation of DR 28 by simultaneously applying semiconductor heterogeneous photocatalysis with plasma. We also plan to identify RO 16, RB 19, and DR 28 oxidation by-products and determine their toxicity level. Future work is planned in enhancing present methodology by using the design of experiments, which will contribute to obtaining dataset more suitable for multidimensional interpolation.

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SUPPLEMENTARY MATERIAL

Supplementary Material is available electronically from the journal web site: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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SUPPLEMENTARY MATERIAL TO

ANN prediction of decolourisation efficiency of organic dyes in wastewater by plasma needle

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TABLE SI. ANN structure and performance used for prediction of the decolourisation process for textile dyes RO 16, RB 19 and DR 28

<table>
<thead>
<tr>
<th>Dye</th>
<th>RO 16</th>
<th>RB 19</th>
<th>DR 28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of neurons per layer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Input layer</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Pattern layer</td>
<td>40</td>
<td>34</td>
<td>77</td>
</tr>
<tr>
<td>Summation layer</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Output layer</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Performance metrics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMSE¹</td>
<td>0.045</td>
<td>0.091</td>
<td>0.055</td>
</tr>
<tr>
<td>MAE²</td>
<td>0.027</td>
<td>0.077</td>
<td>0.037</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dataset</th>
<th>Training</th>
<th>Validation</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data points</td>
<td>40</td>
<td>34</td>
<td>77</td>
</tr>
</tbody>
</table>

¹Root Mean Square Error, ²Mean Absolute Error

TABLE SIIa. Descriptive statistics of the model for entire dataset and created subsets for RO 16

<table>
<thead>
<tr>
<th>Input</th>
<th>Training</th>
<th>Validation</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>S E³</td>
<td>Min</td>
</tr>
<tr>
<td>t / min</td>
<td>24.9</td>
<td>3.5</td>
<td>0</td>
</tr>
<tr>
<td>Q / dm³ min⁻¹</td>
<td>4.1</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>O₂ content, %</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>A/A₀⁵</td>
<td>0.38</td>
<td>0.05</td>
<td>0.00</td>
</tr>
</tbody>
</table>
### TABLE SIIb. Descriptive statistics of the model for entire dataset and created subsets for RB 19

<table>
<thead>
<tr>
<th>Input</th>
<th>Training</th>
<th>Validation</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M^a$</td>
<td>$S. E^b$</td>
<td>Min</td>
</tr>
<tr>
<td>$t$ / min</td>
<td>18.5</td>
<td>3.4</td>
<td>0</td>
</tr>
<tr>
<td>$Q$ / dm$^3$ min$^{-1}$</td>
<td>4.2</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>$O_2$ content, %</td>
<td>0.01</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>$A/A_0$</td>
<td>0.41</td>
<td>0.06</td>
<td>0.00</td>
</tr>
</tbody>
</table>

### TABLE SIIc. Descriptive statistics of the model for entire dataset and created subsets for DR 28

<table>
<thead>
<tr>
<th>Input</th>
<th>Training</th>
<th>Validation</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M^a$</td>
<td>$S. E^b$</td>
<td>Min</td>
</tr>
<tr>
<td>$t$ / min</td>
<td>68.4</td>
<td>79.6</td>
<td>0</td>
</tr>
<tr>
<td>$Q$ / dm$^3$ min$^{-1}$</td>
<td>4.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$O_2$ content, %</td>
<td>0.03</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>$A/A_0$</td>
<td>0.39</td>
<td>0.30</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*Mean Value; $^b$ Standard Error; $^c$ Model output

### REFERENCES