The use of artificial neural network for modeling the decolourization of acid orange 7 solution of industrial by ozonation process

S Fatimah¹ and W Wiharto²

¹Department of Chemical Engineering, Muhammadiyah University of Surakarta, Indonesia
²Department of Informatic, Sebelas Maret University, Indonesia

E-mail: sf120@ums.ac.id

Abstract. Acid Orange 7 (AO7) is one of the synthetic dye in the dyeing process in the textile industry. The use of this dye can produce wastewater which will be endangered if not treated well. Ozonation method is one technique to solve this problem. Ozonation is a waste processing techniques using ozone as an oxidizing agent. Variables used in this research is the ozone concentration, the initial concentration of AO7, temperature, and pH. Based on the experimental result that the optimum value decolourization percentage is 80% when the ozone concentration is 560 mg/L, the initial concentration AO7 is 14 mg/L, the temperature is 390 °C, and pH is 7.6. Decolourization efficiency of experimental results and predictions successfully modelled by the neural network architecture. The data used to construct a neural network architecture quasi newton one step secant as many as 31 data. A comparison between the predicted results of the designed ANN models and experiment was conducted. From the modeling results obtained MAPE value of 0.7763%. From the results of this artificial neural network architecture obtained the optimum value decolourization percentage is 80.64% when the concentration of ozone is 550 mg/L, the initial concentration AO7 is 11 mg/L, the temperature is 41 °C, and the pH is 7.9.

1. Introduction

Many industries use dyes and pigments to colourize their products. Some dyes with concentrations that they are discharged to the environment, are often non-poisonous, however, they give undesirable perspective to the water streams [1], whereas, some other dyes are poisonous and carcinogen and cause severe toxicity for aqueous microorganisms [2]. Dyes also can prevent from photosynthesis in aqueous ecosystems by absorbing sunlight. It is important to know that weaving industries use large amounts of water and in these industries more than 30–60 L of water per kilogram of dyed fabric is used and large amount of wastewater (16% of used water), is produced [3]. Also, total dye consumption in the weaving world industries is more than 107 kg/year and approximately 10% of this amount, 106 kg, is discharged to water streams [2]. Generally most of these compounds cause mutagenic and carcinogenic effects which subsequently lead to the generation of health disorders such as decreasing function of the kidney, reproductive system, liver, brain, and central nervous system. Dyes according to their charge and nature classified to categories including anionic (direct, acid, and reactive dyes), cationic (basic dyes), and non-ionic (disperse dyes). Among the anionic dyes are the
brightest class of soluble dyes and generate serious environmental and health problems. These hazards and difficulties encourage the researchers to design novel approaches or material for their safe removal and subsequent achievement of clean aquatic environment.

Acid orange 7 (AO7) is one kind of azo dyes, which is widely used in textile industries. However, AO7 is difficult to be degraded by conventional methods due to its non-negligible toxicity, low biodegradability and dark colours. It is a mono azo dye and is widely used in dyeing of synthetic fibre and wool and cotton and in paper industries. Active azo dyes have double bound of nitrogen to nitrogen (–N=N–), which is bounded to an aromatic group so, they can produce harmful health effects and it is essential to have a proper method to remove this dye from wastewaters. The characteristics and structure of acid orange 7 were shown in Table 1.

Table 1. Characteristics and Structure Of Acid Orange 7

| Name             | Chemical structure | Molecular Formula | Colour index number | λ<sub>max</sub> (nm) | M<sub>w</sub> (g/mol) |
|------------------|--------------------|-------------------|---------------------|----------------------|----------------------|
| Acid Orange 7    | ![Chemical Structure](image) | C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>NaO<sub>4</sub>S | 15510               | 484                  | 350.32               |

A broad range of physicochemical methods has been proposed for treatment of dyeing effluents including biological [4], adsorption [5], membrane [6], coagulation-flocculation [7], oxidation-ozonation [8], and advance oxidation process (AOPs) [9][10]. Ozonation, one of the most used AOPs, is an oxidation process in which the oxidizing agent used is ozone (O<sub>3</sub>). Interest in the use of ozone in wastewater treatment has increased considerably in recent years due to the numerous advantages of this process. Among them is the high oxidation potential of ozone even at low concentrations, with its high efficiency in the decomposition of organic matter and in the addition of oxygen to water [11]. Degradation process with ozone proceeds in two different ways, they are direct and radical reaction. At acidic pH, molecular ozone selectively attacks specific parts of organics molecules like double bonds or aromatic systems of reactive dyes in direct reaction. At alkaline pH, hydroxide radicals coming from ozone decomposition react unspecifically with organic compounds[12]. The alkaline to neutral pH of dyeing wastewater favours the unspecific radical reaction. The pH solution may decrease around the dye molecules due to the formation of organic acid such as the ozonation products. Therefore, the reaction mechanism shifts towards the selective direct oxidation [13].

The mechanism of O<sub>3</sub> reaction was studied by Hoigne [12]. Ozone react directly with pollutants via ozonolysis and through radical chain reaction. The reaction of ozone with hydroxide anions to intermediate radicals and to hydroxyl radicals is important for the oxidation of saturated organic compounds where no molecular ozonolysis is possible[14]. The efficiency of colour removal by ozone is dependent on various parameters such as the ozone dosage, initial dye concentration, initial pH, reaction time, and temperature of the solution[15]. In conventional methods used determined the influence of each one of these parameters, experiments were carried out by varying systematically the studied parameters and keeping constant the others. These should be repeated to all the influencing parameters, resulting in an unreliable number of experiments. In order to optimize the value number of experiments with the minimum number of experiments, was employed to find improved or optimal process settings in an efficient use of the experimental data. Using artificial neural network, it is
possible to estimate linear, interaction, quadratic effects of the factors and to provide a prediction model for the responses.

In this work, the experimental system is modelled by using artificial neural networks. The artificial neural network (ANN) is a system of data processing based on the structure of a biological neural system. The prediction with ANN is made by learning of the experimentally generated data or using validated models [16]. The ANN is an artificial intelligence technique that mimics the human brain’s biological neural network in the problem solving processes. Numerous applications of ANN have been successfully conducted to solve environmental problems since it is reliable and robust in capturing the nonlinear relationship between variables in complex system [17] [18] [19]. This novel modeling tool is newly grown and has not been used yet to model adsorption of AO7 using ozonations. It is applicable in most fields of science [20].

2. Material and Method

2.1. Data
In this study, the data used for experiments using the data in a study conducted Kasiri et. al [15]. The data attribute consist of 4 inputs and one output attribute, namely ozone concentrations (mg/L), AO7 concentration (mg/L), the degree of acidity of pH, temperature (°C) and percentage docolorization. Iran

2.1.1. Reagent
Ozone was continuously produced by an ozone generator (model 1000 mg/L, Nano Pakk Sayyal, Iran). The dyes of AO7 were obtained from Azar Paints Company, Tabriz,. Their structure and characteristics are given in Table. Sulphuric acid and sodium hydroxide were of laboratory reagent grade and were obtained from Merck Inc, Darmstadt, Germany.

2.1.2. Ozonation experimental setup
For decolourization process, ozonation was carried out in a batch reactor, 500 mL in volume, equipped with magnetic stirrer and a thermometer. Experimental setup for ozonation batch experiments is shown in figure 1.

![Figure 1. Experimental setup for ozonation batch experiments [15]](image)

2.2. Experimental Design of Artificial Neural Network
Artificial Neural network (ANN) used in this study is backpropagation. Backpropagation neural network algorithms have a lot of training, in this study using a quasi newton one step secant [21]. The algorithm has the ability quickly to achieve convergent in the training process. Neural network back-propagation using supervised training models, so that the model requires that the data used for training in pairs, namely the input and the target. In this study, there are four inputs, namely ozone concentrations (mg/L), AO7 concentration (mg/L), the degree of acidity of pH and temperature (°C),
while the output of the system is the percentage decolourization. The training process is done by making changes to the weights ANN order to obtain output corresponding to the target used in training. Changes in weight training ANN with quasi Newton algorithm can be written in equation (1) below

$$W_{k+1} = W_k - A_k^{-1} \cdot gW_k$$  \hspace{1cm} (1)

Where $A_k$ is the Hessian matrix, $W_k$ is the k-th weighting. The algorithm does not perform a complete storage for hessian matrix, assuming that at each iteration, the previous hessian matrix is the identity matrix. This makes the training process becomes faster and does not require a large memory. Architecture of artificial neural network backpropagation with two hidden layers can be shown in figure 2.

![Neural Network Architecture System](image)

**Figure 2. Neural Network Architecture System**

In this study, to model percentage decolorisation using artificial neural network is divided into three processes, namely normalization and denormalize the data (preprocessing and post processing), training and testing. The process of normalization of data is done to bring the value of the input attributes to within a certain range, and normalize the output side of the neural network to return values into their original range. In this study, using methods preprocessing and postprocessing mean and standard deviation. The next stage is done training the neural network. Training is done by using a neural network optimization algorithms backpropogation with one step secant quasi newton. The algorithm is an alternative conjugate gradient to get the optimum value faster. The training process is done repeatedly, in order to obtain an optimum architecture. Furthermore, the last stage of testing of the system.

2.3. Evaluation Parameters

The performance evaluation were performed using SPSS version 23 for test of significance with 95% confidence level. In addition, it is also used to test the Mean Absolute Percentage Error (MAPE) is the absolute value of the data about the mean percentage error. The test to determine the ability of a neural network in doing prediction. The test can be formulated in equation (2) below

$$MAPE = \frac{\sum_{i=1}^{n} |\text{decolorization predicted} - \text{decolorization experimental}|}{\text{decolorization experimental}} \times 100\%$$  \hspace{1cm} (2)
After the evaluation of performance of the neural network, the neural network architecture that is produced is used to obtain the optimum value AO7 dye decolourization process.

3. Result and Discussion

One effective technique in the process of decolourization of waste containing dye AO7 is by Advance Oxidation Process (AOPs) or ozonation. The reaction mechanism of ozonation process has been studied by Hoigne [12]. In his research explained that the process of ozonation, ozone reacts with pollutants directly through ozonolysis process. This process involves a radical chain reaction of pollutants. The reaction between ozone with the hydroxide radical anion intermediates. These hydroxyl radicals that play an important role in degraded the pollutants. Illustration of hydroxyl radical formation can be described by equation (3-5) follows:

\[
O_3 + UV (or \ h \nu < 310 \ nm) \rightarrow O_2 + O(D^1) \tag{3}
\]
\[
O(D^1) + H_2O \rightarrow HO\bullet (\text{wet condition}) \tag{4}
\]
\[
O(D^1) + H_2 \rightarrow HO\bullet + HO\bullet \rightarrow H_2O_2 (\text{in water}) \tag{5}
\]

Decomposition of ozone due to sunlight in the damp air will produce active hydroxyl radicals. In the process of water tend to form hydrogen peroxide, so it would be more effective if the compound to be degraded have good absorption to UV light. Factors that affect the process ozonolysis on decolourization AO7 these include the concentration of ozone is used, the concentration of the dye AO7, pH and temperature. To produce hydroxyl radicals that can decolourise AO7 waste it is necessary also sufficient for the amount of ozone decolourization process. The greater the percentage of ozone concentration of ozone dissolved in water will also increase, this will lead to the ability to oxidize AO7 even greater. The solubility of ozone in the lower water temperature rises, this reaction is endothermic [22].

Modeling percentage decolourization AO7 has been successfully done using Artificial Neural Network. Artificial neural network architecture that is generated with reference to figure 2, comprising a number of input overcome four attributes, two hidden layers and one output layer. The hidden layer consists overcome 30 neurons in the first hidden layer and 25 neurons in the second hidden layer. The activation function used is tansig, logsig and purelin. Based on the test results showed that percentage decolourization resulting from ANN is not much different from the experimental results, as shown in table 2. In the Table shows the test results p-value > 0.05 which showed there was a significant difference between the prediction by the neural network with experiment.

| Table 2. Test Significance Model ANN at Percentage Decolourization |
|---------------------------------------------------------------|
| Paired Differences | 95% Confidence Interval |
|                   | Std. Deviation | Mean | Std. Error | Lower | Upper | t      | df | Sig. (2-tailed) |
| Pair 1 | Experimental – Predicted | 0.00000 | 1.06458 | 0.19120 | -0.39049 | 0.39049 | 0.000 | 30 | 1.000 |

ANN system testing, in addition to using t-test significance test, also using MAPE. The test results demonstrate the value with MAPE 0.7763%. MAPE value of less than 10% in the case of prediction can be tolerated. It can also be shown graphically percentage decolourization value of prediction and experiment result, as shown in figure 3. Artificial neural network model generated with reference to the results of performance testing with two parameters, namely the significance test t-test and the value of MAPE, artificial neural network model meets the criteria to be used in the prediction percentage decolourization the case of AO7 dye.
By using architectural ANN 2 hidden layer testing is done to obtain optimum percentage decolourization. Testing by many as 14625 of data (results generated) values obtained percentage decolourization as shown in table 3. Results of optimum percentage decolourization not much different from that produced by the experiment. Based on the experiments showed that the percentage of decolourization AO7 by 80% with the condition of the ozone concentration of 500 mg/L, AO7 concentration of 14 mg/L, pH 7.6, and the temperature 39 °C. While predictions using ANN produce AO7 decolourization percentage of 80.64% with the condition of the ozone concentration of 550 mg/L, AO7 concentration of 11 mg/L, pH 7.9, and a temperature of 41 °C. This difference is caused by several things. First, the variable ozone concentration, pH and temperature. If the concentration of ozone increases then the temperature will increase the interaction between molecules of ozone increases. As an impact is the kinetic energy of the compound in solution will also increase. The increase of activation energy has resulted in the number of hydroxyl ions produced from the oxidation process increases. The existence of the number of hydroxyl ions will cause the pH to rise. Same with the research that has been conducted by Lu et.al [23] that the degradation of azo dyes effectively carried out under alkaline pH for hydroxyl radicals oxidizing properties will have an optimum at alkaline conditions. The second difference is the initial concentration AO7 variables. If the initial concentration of the lower AO7 it will produce increasingly higher percentage decolourization due to the presence of molecules of AO7 slightly. This affects the number of molecules AO7 oxidized by hydroxyl radicals. The ability of hydroxyl radicals as the oxidizing molecules will increase due to the availability AO7 slightly.

Table 3. Decolourization Efficiency at Optimum Values of The Process Parameters.

| Ozone concentration (mg/L) | Initial dye concentration (mg/L) | Initial pH | Temperature (°C) | % decolourization |
|----------------------------|---------------------------------|------------|------------------|-------------------|
| Experimental               | 500                             | 14         | 7.6              | 39                | 80.00             |
| Predicted                  | 550                             | 11         | 7.9              | 41                | 80.64             |

Similar to the research that has been done by Kasiri et.al [15] whereas in the study the percentage of decolourization AO7 modeling using surface method area produces AO7 decolourization percentage of 77.9%. In this study, the use of ANN as modeling AO7 decolourization AO7 able to produce a percentage of 80.64%. This shows that the use of ANN is better than the surface method area to model the percentage of decolourization AO7.
To determine the level of confidence or significance of this modeling, the test statistic by using t-test. In the t-test which will be compared between the experimental results and predictions. If the p-value was greater than 0.05, it can be concluded that between the experiment and the predictions are not much different. The results of significance test by using t-test shown in table 4, where the p-value 0.376, or p-value > 0.05.

| Table 4. Test Significance Prediction with ANN and Experiment |
|------------------------------------------------------------|
| Paired Differences                                         |
|                                                          |
| Mean | Deviation | Mean | Lower | Upper |
|-------|------------|-------|-------|-------|
| Pair 1 | Experimental – Predicted | -9.9880 | 22.4427 | 10.0366 | -37.8542 | 17.8782 | -0.995 | 4 | 0.376 |

4. Conclusion
Model predictions using neural networks to predict the percentage of decolourization AO7 able to deliver results that are not much differ significantly with experimental results. This is indicated by the p-value between experiment and prediction generated is equal to 0.376. Under these conditions, the percentage of decolourization AO7 modeling can be done using ANN.

5. References
[1] Annadurai G, Juang J, and Lee D 2004 Use of cellulose-based wastes for adsorption of dyes from aqueous solutions J. Hazard. Mater. 92 263–74.
[2] Wong Y, Szeto Y, Cheung W, and McKay G 2004 Adsorption of acid dyes on chitosan-equilibrium isotherm analyses Process Biochem. 39 695–704.
[3] Sivaraj R, Namasiyvayam C, and Kadirvelu K 2000 Orange peel as an adsorbent in the removal of Acid violet 17 (acid dye) from aqueous solutions Waste Manag. 21 105–110.
[4] Khataee A and Kasiri M 2011 Modeling of Biological Water and Wastewater Treatment Processes Using Artificial Neural Networks CLEAN-Soil Air Water 39 742–749.
[5] Clercq J 2012 Removal of mercury from aqueous solutions by adsorption on a new ultra stable mesoporous adsorbent and on a commercial ion exchange resin Int. J. Ind. Chem. 3 1–6.
[6] Harrelkas F, Azizi A, Benhammou A Y, and Pons M 2009 Treatment of textile dye effluents using coagulation–floculation coupled with membrane processes or adsorption on powdered activated carbon Desalination 235 330–339.
[7] Salari D, Niaei A, Khataee A, and Zarei M 2009 Electrochemical treatment of dye solution containing C.I. Basic Yellow 2 by the peroxi-coagulation method and modeling of experimental results by artificial neural networks J. Electroanal. Chem. 629 117–125.
[8] Saruyu K, Swaminathan K, and Sandhya S 2007 Assesment of Degradation of Eight Commercial Reactive Azo Dyes Individually and in Aqueous Solution by Ozonation Dyes Pigments 75 362–368.
[9] Kasiri M and Khataee A 2012 Removal of organic dyes by UV/H2O2 process: modeling and optimization J. Environ. Technol. 33 1417–1425.
[10] Rasoulifard M, Majidzadeh H, Demneh F, Babaei E, and Rasoulifard M 2012 Photocatalytic degradation of tylosin via ultraviolet-activated persulfate in aqueous solution Int. J. Ind. Chem. 16 1–6.
[11] Souza S M A G, Bonilla K A S, and Souza A A 2010 Removal of COD and color from
hydrolyzed textile azo dye by combined ozonation and biological treatment J. Hazard. Mater. 179 35–42.

[12] Hoigne J 1988 Chemistry of Aqueous Ozone and Transformation of Pollutants by Ozonation and Advanced Oxidation Process (Berlin: Springer).

[13] Kornmuller A, Karcher S, and Jekel M 2001 Cucurbituril for water treatment. Part II:: Ozonation and oxidative regeneration of cucurbituril Water Res. 35 3317–3324.

[14] Chu L B, Xing X H, Yu A F, Sun X L, and Jurcik B 2008 Enhanced treatment of practical textile wastewater by microbubble ozonation Process Saf. Environ. Prot. 86 389–393.

[15] Kasiri M B, Modirshahla N, and Mansouri H 2013 Decolourization of organic dye solution by ozonation; Optimization with response surface methodology Int. J. Ind. Chem. 4 1–10.

[16] Fagundes-Klena M R, Ferria P, Martins T D, Tavaresb C R G, and Silvaa E A 2007 Equilibrium study of the binary mixture of cadmium–zinc ions biosorption by the Sargassum filipendula species using adsorption isotherms models and neural network Biochem. Eng. J. 34 136–146.

[17] Turan N G, Mesci B, and Ozgonenel O 2011The use of artificial neural networks (ANN) for modeling of adsorption of Cu(II) from industrial leachate by pumice Chem. Eng. J. 1711091–1097.

[18] Aber S, Amani-Ghadim A R, and Mirzajani V 2009 Removal of Cr(VI) from polluted solutions by electrocoagulation: Modeling of experimental results using artificial neural network J. Hazard. Mater. 171 484–490.

[19] Salari D, Daneshvar N, Aghazadeh F, and Khataee A 2005 Application of artificial neural networks for modeling of the treatment of wastewater contaminated with methyl tert-butyl ether (MTBE) by UV/H2O2 process J. Hazard. Mater. 125 205–210.

[20] Aber S, Daneshvar N, Soroureddin S, Chabok A , and Asadpour-Zeynali K 2007 Study of acid orange 7 removal from aqueous solutions by powdered activated carbon and modeling of experimental results by artificial neural network Desalination 211 87–95.

[21] Wiharto, Aziz A, and Permana U 2015 Improvement of Performance Intrusion Detection System (IDS) Using Artificial Neural Network Ensemble J. Theor. Appl. Inf. Technol. 80 191-201.

[22] Nugroho R and Ikbal 2005 Pengolahan air limbah berwarna industri tekstil dengan menggunakan teknik AOPs JAI 1163–172.

[23] Lu X, Yang B, Chen J, and Sun R 2009 Treatment of wastewater containing azo dye reactive brilliant red X-3B using sequential ozonation and upflow biological aerated filter process J. Hazard. Mater. 161 241–245.