Multiple linear regression for the analysis of the parameters used in dyes decolourisation by ozonation techniques

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Abstract. The ozonation process of dye Acid Orange 7 (AO7), Acid Yellow 19 (AY19), and Acid Black 1 (AB1) have been performed. The experimental results predicted the magnitude of the influence of each variable by using Multiple Linear Regression (MLR). This process produces predictive modeling of the variables studied. The variables studied in this ozonation process are independent variables consisting of ozone concentration (mg/L), concentration of dye (mg/L), pH and temperature (⁰C). The dependent variables studied were the percentage of dye decolorization. The feasibility of the prediction model used has also been tested using the t-test. Based on the prediction model, R² values for AO7, AY19, and AB1 dyes are 0.84, 0.87, and 0.93 respectively. The analysis of the influence of the independent variables on the percentage of dye decolorization predicted that the concentration of ozone, dyestuff concentration and pH, significantly influenced the ozonation process of AO7, AY19, and AB1. In the ozonation process the temperature variables have a significant effect on AY19 and AB1, but stronger influence on AO7 ozonation process. Based on the predictions of the influence of each variable, the process in the laboratory can be optimized more effectively and efficiently, so that the cost and time factor can be reduced.

1 Introduction

The industrial world produces liquid waste resulting from its industrial activities. Paper, pulp, cosmetics, paint, printing, leather, pharmaceuticals, beauty and plastics industries are some of the industries that use synthetic dyes [1]. The use of dye in the process will result in hazardous waste which can endanger life. The dyes used in industrial processes can be classified into two groups, i.e. azo and non-azo groups, where the differences between the two is the presence of the azo group (-N = N-). An azo dye has azo groups that can be more than one. While non-azo dye does not have any azo group. Mostly, azo dyestuffs are more widely used than non-azo groups. This is because the azo dye has a complex structure, so that stabilize the staining

process, and the product does not quickly fade [2]. Some commonly used azo dyestuffs include Acid Black 1 (AB1), Acid Yellow 19 (AY19), and Acid Orange 7 (AO7) [3]. The characteristics of the three dyestuffs are presented in Table 1.

Through simple handling, azo dyes contained in textile industry waste are very difficult to process, so that appropriate techniques are needed. Currently various techniques for handling textile waste are being developed so that the waste that comes out of the industry is not harmful to the life of water biota. Azo dye waste discharged into rivers or aquatic ecosystems is capable of influencing water transparency, which affects the penetration of sunlight from rivers. Furthermore, they can also be toxic and mutagenic to organisms or aquatic biota.

Table 1. Dye Characteristics

Dyes	Structure	Formula	Mono/diazo	$\lambda_{\max}$ (nm)	M _w (g/mol)
Acid Orange 7		C ₁₆ H ₁₁ N ₂ NaO ₄ S	Monoazo	484	350,32
Acid Yellow 19		C ₂₀ H ₁₂ Cl ₂ N ₄ Na ₂ O ₇ S ₂	Monoazo	401	551,29

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Acid Black 1		C ₂₂ H ₁₄ N ₆ Na ₂ O ₉ S ₂	Diazo	618	616,49
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To overcome the problem, an effective and an efficient technique are needed. One of the techniques currently under development is the use of Advance Oxidizing Process [1]. The Advanced Oxidation Process (AOPs) method has the main advantage of being able to degrade / completely separate nonbiodegradable hazardous compounds in waste through oxidation [2]. This technique uses chemicals such as oxidizing agents or reducing agents as a treatment based on the formation of hydroxyl radicals produced in the oxidation process. Some examples of research that have used this technique are the use of ozone [3], fenton and sono-fenton [4], persulfate-hydrogen peroxide [1], combination of ozone and electrolysis [5], peroxydisulfate [2], non-thermal AOPs (Advanced Oxidation Process) [6], photocatalyst-zerovalent/copper [7], UV/H₂O₂ [8]. The AOPs technology is a combination of several process to produce free hydroxyl radicals (•OH). These hydroxyl radicals are selective against pollutants so that they are effectively used to handle textile industry waste. Ozone has a high oxidation rate of 2.08 V so that it can produce free hydroxyl radicals (•OH). The hydroxyl radicals is considerable powerful to oxidize both organic and non-organic compounds [1].

Some of the variables that affect the degradation efficiency using ozonation include pH, initial concentration of dyestuff, ozone concentration, and temperature. The dye AO7, AY19 and AB1 have different amount of azo bonds, AB1 has two azo bonds while AO7 and AY19 have one azo bond. These differences in the number of azo groups will affect the degradation efficiency of the dyestuff under the same treatment conditions. It has also been investigated using artificial neural network modeling (ANN) by Fatimah et.al [9] that the difference in the number of azo bonds present in the dye affects the percentage of decolorization. In acidic conditions, the ozone molecule is highly selective in attacking the active group of the dyestuff, such as the presence of double bonds or aromatic groups present in the dyestuff. In the basic conditions of hydroxyl radicals are produced from the process of decomposition or decomposition of the dyestuff itself. Under alkaline pH conditions up to neutral pH, there may be reactions which cannot produce radical reactions of hydroxyl formation. The pH value of the solution will decrease with the formation of the hydroxyl compound from the ozonation process. The reaction mechanism of the ozonation process is that the ozone reacts directly with the dyestuff through the ozonolysis process and through the formation of a radical chain. The reaction between ozone and anion hydroxide to intermediate radicals and hydroxyl radicals is essential in the oxidation process of this dye [10].

The degradation efficiency of the ozonation process can be done systematically by testing each variable by making the other variable fixed. This is done repeatedly for several times to produce maximum efficiency. Repetition of this experiment will require time and it can be very costly. The prediction on the strength of the influence of the variables of each experiment can be determined so that it can optimize the existence of each variable. To analyze the performance of the degradation process through ozonation, method of analysis of Multiple Linear Regresion (MLR) can be used. MLR analysis investigated a linear relationship between two or more independent variables (X₁, X₂,X_n) with the dependent variable (Y). This analysis is to reveal the direction of the relationship between independent variables and dependent variables, whether each independent variable has positive or negative effects, and to predict the value of the dependent variable if the value of the independent variable increases or decreases [11]. The data used are usually scaled intervals or ratios. This method involved the development of a single or simple regression. This study used independent variables consisting of 4 parameters namely the concentration of ozone (mg/L), concentration of dye (mg/L), pH, and temperature (°C). The dependent variable consists of one parameter only that was the percentage of decolourization (%).

The MLR model of dyestuff decolorization by using adsorption has been performed by Ho et.al [12]. This study only analyzed the data set by using Chi square so that the power between variables were not explained in detail. Another study by Muthukumar et.al [13] describes the effect of active groups on some dyes on COD values using UV/H₂O₂ modeled by statistical tests. To determine the effect of the dye strength on the fabric have been modeled with MLR also by Timofei et.al [14] and Wang et.al [15]. The MLR application is also used by Yao et.al [16] to find out how much the molecular structure affects molecular activity.

Referring to the previous research, it was proposed to use MLR to find out how much influence of each of the variables in the process of dye decolourization in ozonation. From the results of this analysis, it could be known which variables were the most dominant influence so that it would become possible to manage the time and costs in waste processing.

2 Material and Method

2.1 Material

In this study the data used were secondary data obtained from research that has been done by Kasiri

et.al [17]. The parameters used in analyzing this model consisted of 4 parameters as the independent variable and 1 parameter as the dependent variable. Independent variables consisted of ozone concentration (mg/L), concentration of dye (mg/L), pH, and temperature (°C). The dependent variable consisted of the percentage value of decolorization.

2.2 Experimental design

Secondary data obtained was processed by using software SPSS version 23. In this research Multiple Linear Regression analysis (MLR) was used. The advantages of using the MLR was that we are able to determine how much influence of independent variables to dependent variables. MLR model can be written in Equation 1. In the design of this study each variable is encoded into a symbol that it was so easy to interpret.

$$Y = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_2 + \alpha_3 X_3 + \alpha_4 X_4 \quad (1)$$

Explain:

- Y : Percentage of decolorisation (%)
- α_0 : Constanta or Determination Coefficients
- α_1 : Coefficient regression for ozone concentration
- α_2 : Coefficient regression for dyes concentration
- α_3 : Coefficient regression for pH
- α_4 : Coefficient regression for temperature
- X_1 : ozone concentration (mg/L)
- X_2 : dyes concentration (mg/L)
- X_3 : pH
- X_4 : temperature (°C)

2.3 Parameter analysed

The determination analysis in multiple linear regression is used to know the percentage of contribution of independent variables ($X_1, X_2, X_3, \dots, X_n$) simultaneously to the dependent variable (Y). This coefficient shows how much percentage of variation of independent variable used in the model was able to explain variation of dependent variable. The value of R^2 equals 0, so there was no percentage contribution of the influence given by the independent variable to the dependent variable, or the variation of the independent variable used in the model did not explain the slightest variation of the dependent

variable. On the contrary, when R^2 equals 1, the percentage of contribution given by the independent variable to the dependent variable is perfect, or the variation of the independent variable used in the model explains 100% variation of the dependent variable. This experiment also analyzed ANOVA from each of the equations obtained. If the significance value of ANOVA <0.05 then the regression equation used is feasible. To find out which variable is most influential and the possibility of unused variable then used enter method, which putting all the variables into the analysis at once [11].

3 Result and Discussion

The AOPs (Advance Oxidation Process) technique involves oxidation reactions sourced from ozone (O_3) in solution to produce free hydroxyl radical $\bullet OH$. This hydroxyl radical has a very large role in oxidizing the dye so that it can decrease the presence of the dyestuff. Ozone has an unstable oxygen element, so it is very reactive. This can be explained in the following reaction:

Species of $\bullet O$ is radical so that when it collided with water, it will form hydroxyl ions ($OH^\cdot$), thus forming a radical $\bullet OH$, which in turn will play a role in overhauling the bonds of the dyestuff compounds.

Parameters used in this ozonation process are ozone concentration (mg/L), concentration of dye (mg/L), pH and temperature (°C). Each variable parameter has an influence with different dominance. To know how was the big influence of each variable, this was done by MLR analysis. Based on the MLR equation using the enter method, the data obtained as shown in Table 2. As shown on Table 2, the obtained values of R^2 for AO7, AY19, AB1 are equal to 0.84, 0.87, and 0.93. This shows that the effect of free variable to the percentage value of dye decolorization are 84%, 87%, and 93% respectively. The rest of the whole 100% value are the influence of other than ozone concentration, dye concentration, pH, and temperature. The p-value of the ANOVA test of each dye is <0.005 . This indicates that this regression equation could be used to analyze the influence of independent variable to decolorization percentage. The regression equation for each dye is shown in Table 2.

Table 2. The Result of Statistical MLR Equations

Dyes	R^2	Sig.ANV	Regression equation
AO7	0,84	0,000	$Y = 23,328 - 0,001X_1 - 0,650X_2 + 4,556X_3 + 6,50X_4$
AY19	0,87	0,000	$Y = 49,473 + 0,005X_1 - 0,708X_2 + 4,167X_3 + 0,46X_4$
AB1	0,93	0,000	$Y = 73,546 + 0,006X_1 - 0,775X_2 + 7X_3 - 0,483X_4$

Based on the correlation significance test in Table 3, it was found that in the ozonation process of AO7, the influence of concentration O_3 exert a relatively small effect on this process. The most influential variables in this process are the concentration of AO7, pH and temperature. It can be explained that for the addition of 1 mg/L of dye concentration, with increased the pH conditions and increased in temperature, will increase the percentage of decolorization. The resulting hydroxyl radical can increase the effectiveness of decolorization. In the process of analysis of the effect of independent variables on ozonation AY19, it was obtained that the concentration variable AY19 and pH is the variable that gave the most significant influence.

With the increase in pH then the percentage of decolorization will be greater. It can be explained that in AY19 there are two sulphonic acid groups and the presence of chlorine and methyl groups. The presence of these constituents will affect the formation of hydroxyl radicals. In the process of ozonation AB1 the most influential variable is the concentration of AB1, pH, and temperature. AB1 structure contains two sulphonic acid groups, one nitro and amine group. This, of course, affects the presence of hydroxyl radicals resulting from the ozonation process. The more the amount of substituents in the dye causes the decolorization process to become more challenging and require the other variable to be more effective.

Table 3. The Significance of Correlation

Dye	Parameters	Correlation				
		$[O_3]$	[dye]	pH	T	Constanta
AO7	p-value (Sig.)	0,845	0,000	0,000	0,016	0,55
	t	-0,197	-5,133	5,396	2,567	2,013
AY19	p-value (Sig.)	0,403	0,000	0,000	0,112	0,000
	t	0,850	-5,272	7,143	-1,644	5,466
AB1	p-value (Sig.)	0,164	0,000	0,000	0,005	0,000
	t	1,434	-9,373	8,271	3,088	7,513

The resulting analysis showed that the pH factor played a most significant role in the ozonation processes of AO7, AY19, and AB1. In acidic pH the ozone is available as molecular ozone and in alkaline pH it decomposes into secondary free radicals such as $\bullet OH$ and $\bullet HO_2$ [18].

Even though hydroxyl radical has a higher oxidation potential than ozone its selectivity is much less. The oxidizing potential of ozone decrease from 2,8V in acidic pH to 1,4V in alkaline solution. This indicates that the ozone stability decrease with increasing pH, it results in the generation of secondary free radicals.

4 Conclusion

Analysis of the effect of free variables on dye decolorization of AO7, AY19, and AB1 can use Multiple Linear Regression method. This MLR equation is effective in determining the most significant independent variables affecting the dye decolorization process. Based on the analysis, the variable of dyestuff concentration and pH is the most influential factor on this process. Temperature variables significantly influence the decolorization of AY19 and AB1, whereas at AO7 the temperature

variables have more significant effect. This equation can be conditioned for laboratory research so that it can be regulated by technical procedures that affect time and cost.

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