ADSORPTION OF ACID VIOLET 7 DYE USING RHA/CFA SORBENT: MODELLING, PROCESS ANALYSIS AND OPTIMIZATION

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by

NG WEI LING

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LIST OF SYMBOLS

Symbol	Description	Unit
C_{in}	Initial Concentration	mg/L
i	Component Index	-
m	Total Number of Levels in the Design	-
N	Number of Variable	-
n_i	Number of Observations	-
p	Number of Parameter of Model	-
pH_{in}	Initial pH	-
R	Coefficient of Correlation	-
R^2	Coefficient of Determination	-
T	Temperature	℃
x	Experimental Factor	-
x_n	Normalized Experimental Factor	-
y_{exp}	Experimental Response	-
y_n	Normalized Experimental Response	-
y_{pre}	Predicted Response	-
$\hat{y}_i$	Estimated Value by the Model for Level i	-
$\bar{y}$	Overall Media	-
y_{ij}	Replicates Performed in Each Individual Levels	-
$\bar{y_i}$	Media Of Replicates Performed in the Same Set of Experimental Conditions	-
β_0	Constant Term	-
β_i	Coefficients of Linear Parameters	-

β_{ij}	Coefficients of Interaction Parameters	-
β_{ii}	Coefficients of Quadratic Parameter	-
ϵ	Residual Associated to the Experiments	-

LIST OF ABBREVIATIONS

4"-AA	4’-aminoacetanilide
5-ANDS	5-acetamido-2-amino1-hydroxy-3,6-naphtalene disulfonic acid
ADMI	American Dye Manufacture Institute
ANN	Artificial Neural Network
ANOVA	Analysis of Variance
AV 7	Acid Violet 7
BBD	Box–Behnken Design
BOD	Biochemical Oxygen Demand
CCD	Central Composite Design
CFA	Coal Fly Ash
COD	Chemical Oxygen Demand
CV	Crystal Violet
DNA	Deoxyribonucleic Acid
DOE	Department of Environment
MLP	Multi-layer Perceptron
MRE	Mean Relative Error
MS	Media of Square
MSE	Mean Squared Error
RHA	Rice Husk Ash
RMSE	Root Mean Squared Error
ROS	Reactive Oxygen Species
RSM	Response Surface Methodology
SS	Sum of Square

PENJERAPAN PEWARNA ASID VIOLET 7 DENGAN MENGGUNAKAN BAHAN PENJERAP RHA/CFA: PEMODELAN, ANALISIS PROSES DAN PENGOPTIMUMAN

ABSTRAK

Faktor-faktor yang mempengaruhi prestasi penjerapan asid violet 7 (AV 7) telah dianalisiskan, termasuklah nisbah abu sekam padi (RHA)/abu terbang arang batu (CFA), jenis aditif yang digunakan, dan kepekatan aditif. Eksperimen telah dijalankan berdasarkan reka bentuk tiga-peringkat faktorial dalam kaedah permukaan sambutan (RSM). Hasil dari eksperimen telah digunakan untuk menganalisis pengaruh faktor input pada penjerapan pewarna dan untuk membina model yang dapat meramalkan prestasi sistem penjerapan. Plot permukaan tindak balas mencadangkan bahawa penjerapan pewarna yang cekap boleh dicapai pada nisbah abu dan kepekatan aditif yang tinggi. Model matematik telah dibina dengan menggunakan RSM dan prestasi model dianalisis melalui analisis varians (ANOVA). Model rangkaian neural juga dibina dengan menggunakan peralatan rangkaian neural dalam Matlab, dan juga operasi rangkaian (net operation) dan fungsi peramal (predictor function) dalam Mathematica. Model matematik dan rangkaian neural digunakan untuk meramalkan prestasi penjerapan AV 7. Disebabkan data eksperimen yang terhad untuk latihan rangkaian neural, model matematik yang dijanakan dalam RSM mempunyai ketepatan yang lebih tinggi dalam meramalkan kecekapan penjerapan pewarna AV 7 , dengan nilai R^2 dari 0.9336 dan RMSE dari 3.3515. Pengoptimuman berangka untuk penjerapan AV 7 telah dilakukan oleh RSM untuk mendapatkan keadaan operasi optimum untuk proses penjerapan mencapai kecekapan maksimum. Hasil daripada pengoptimuman menunjukkan kecekapan penjerapan maksimum (45.14%) akan dicapai pada nisbah abu RHA/CFA sebanyak 3.00 dan 1 M NaOH.

ADSORPTION OF ACID VIOLET 7 DYE USING RHA/CFA SORBENT: MODELLING, PROCESS ANALYSIS AND OPTIMIZATION

ABSTRACT

The factors affecting the performance of acid violet 7 (AV 7) adsorption were analyzed, which includes the rice husk ash (RHA)/coal fly ash (CFA) ash ratio, type of additives used, and concentration of additives. The experiment was run based on the 3-level factorial design in response surface methodology (RSM). The experimental results were used to analyze the effect of input factors on dye adsorption and to build a model to predict the performance of the system. Response surface plot suggested that higher dye adsorption efficiency can be achieved at higher ash ratio and higher additive concentration. Mathematical model was built using RSM and the performance of the model was analyzed through analysis of variance (ANOVA). Another neural network model were also built by using neural network toolbox in Matlab, and net operation and predictor function in Mathematica. The mathematical and neural network model were used to predict the performance of AV 7 adsorption. Due to the limited experimental data available for neural network training, mathematical model generated in RSM had better accuracy in predicting the output response. , with R^2 of 0.9336 and RMSE of 3.3515. Numerical optimization for AV 7 adsorption was done by RSM to obtain the optimum operating condition for adsorption to achieve maximum dye removal efficiency. It was found out that the maximum adsorption efficiency (45.14%) would be achieved at RHA/CFA ash ratio of 3.00 and 1 M of NaOH.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Dyes are substances used to color something. They are widely used in textile, leather, paper and plastic industries to make their products more attractive. Dyes can be obtained naturally or synthesized.

Textile industry is the industry that utilize largest amount of water and dyes (Kant, 2012). The wastewater effluent from textile industry contains large amount of dye pollutants. Water contaminated with dyes is undesirable as it will colorize, reduce transmittance of sunlight and oxygen solubility in water bodies and hence affect the aquatic ecosystem (Balköse et al., 2014;Copello et al., 2011). Besides, most of the synthetic dyes are highly toxic and carcinogenic and this will lead to health problem if the contaminated water is being consumed (Rodrigo Otávio et al., 2007;Mathur et al., 2012). Hence the wastewater contaminated with dye pollutants must be treated before it is discharged to the environment or reused in the process.

It is reported that the overall apparel consumption is projected to increase from 62 million tonnes in 2015 to 102 million tonnes in 2030 (Fibre2Fashion, 2017), while around 150 liters of water is required to produce one kilo of textile material or equivalent of one day's attire for one person (Russell, 2018). With the increasing demand on the clothing, the textile production will increase and this will create further environmental stress and risks such as water pollution.

Wastewaters are characterized by many parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, color and salinity. Under Environmental Quality Act 1974, there are rules and regulations especially for the sewage, industrial effluent and leachate discharge. According to Department of Environment (DOE) Malaysia, the acceptable conditions for discharge of industrial effluent for mixed effluent are tabulated in Table 1.1, while the acceptable conditions for discharge of industrial effluent containing COD for specific trade or industry sector are listed in Table 1.2.

Table 1.1: Acceptable conditions for discharge of industrial effluent for mixed effluent (DOE, 2010)

Parameter	Unit	Standard A	Standard B
Temperature	℃	40	40
pH Value	-	6.0 – 9.0	5.5 – 9.0
BOD at 20 ℃	mg/L	20	40
Suspended Solids	mg/L	50	100
Mercury	mg/L	0.005	0.05
Cadmium	mg/L	0.01	0.02
Chromium, Hexavalent	mg/L	0.05	0.05
Chromium, Trivalent	mg/L	0.20	1.0
Arsenic	mg/L	0.05	0.10
Cyanide	mg/L	0.05	0.10
Lead	mg/L	0.10	0.5
Copper	mg/L	0.20	1.0
Manganese	mg/L	0.20	1.0
Nickel	mg/L	0.20	1.0
Tin	mg/L	0.20	1.0
Zinc	mg/L	2.0	2.0
Boron	mg/L	1.0	4.0
Iron (Fe)	mg/L	1.0	5.0
Silver	mg/L	0.1	1.0
Aluminium	mg/L	10	15
Barium	mg/L	1.0	2.0
Fluoride	mg/L	2.0	5.0
Formaldehyde	mg/L	1.0	2.0
Phenol	mg/L	0.001	1.0
Free Chlorine	mg/L	1.0	2.0
Sulphide	mg/L	0.50	0.50
Oil and Grease	mg/L	1.0	10
Ammoniacal Nitrogen	mg/L	10	20
Colour	ADMI*	100	200

**ADMI – American Dye Manufacture Institute*

Table 1.2: Acceptable conditions for discharge of industrial effluent containing chemical oxygen demand (COD) for specific trade or industry sector (DOE, 2010)

Trade/Industry	Unit	Standard A	Standard B
(a) Pulp and paper industry			
(i) Pulp mill	mg/L	80	350
(ii) Paper mill (recycled)	mg/L	80	250
(iii) Pulp and paper mill	mg/L	80	300
(b) Textile industry	mg/L	80	250
(c) Fermentation and distillery industry	mg/L	400	400
(d) Other industries	mg/L	80	200

There are many methods used to treat the wastewater containing dyes. It can be divided into three categories, which are physical, chemical and biological methods. The methods that are commonly used in wastewater treatment in removing dyes are shown in Table 1.3. Among these methods, adsorption is the technique that is widely used in large scale industries due to its low capital, operation costs and simple design (Vital et al., 2016).

Table 1.3: Dye removal methods from wastewater (Vital et al., 2016)

Physical Methods	Chemical Methods	Biological Methods
Adsorption	Fenton reagent Technique	Aerobic degradation
Ion exchange	Ozonisation	Anaerobic degradation
Filtration	Photo-catalytic method	
Coagulation/ flocculation		

Due to the increasing amount of dye-contaminated wastewater generated by the industries, it is needed to have a way that can remove the dyes efficiently and economically in wastewater treatment process. Thus, a proper design of adsorption process in dyes removal is important.

1.2 Problem Statement

Water pollution has become an issue in recent years. The manufacture of textile has increased throughout the years due to the increasing demand on the apparel, such as clothing, bags and shoes. Large amount of water is consumed during the dyeing process. The wastewater effluent from dyeing process contains high concentration of toxic dyes. If the contaminated water is not treated before discharge to the water bodies, it may affect the aquatic system and also lead to human health problem.

Adsorption method is extensively used in wastewater treatment process to remove dyes due to its low capital, operation costs and simple design (Vital et al., 2016). The commonly used adsorbent is the activated carbon. However, the price of activated carbon is relatively expansive. In recent years, many studies are carried out to obtain a low cost adsorbent with high dye removal efficiency. Rice husk ash (RHA) and coal fly ash (CFA) are good options as low-cost adsorbent because they are in abundance and easily available.

RHA and CFA will be mixed in ratio to increase the adsorption capacity. The mixture of RHA and CFA can be in variety of range. Thus, it is necessary to obtain an optimum ratio that can remove the dyes efficiently. Response surface methodology (RSM) and artificial neural network (ANN) are the good choices of computational tools used in determining the cause and effect relationship when there is no mathematical model provided.

On the other hand, the adsorbent is activated by adding the additives, either acid or alkali. The types and concentrations of additive also play an important role in adsorption process. Hence, it is needed to perform optimization to obtain the operating condition that can maximize the efficiency of the process.

In this work, the factors affect the adsorption process of acid violet 7 dyes will be studied and a mathematical model will be developed and used to optimize the process.

1.3 Objectives

The objectives for this research are:

(i) To analyse the effect of type of additives used, additives concentration and RHA/CFA ratio on acid violet 7 adsorption.

(ii) To obtain the empirical statistical model to describe the acid violet 7 adsorption.

(iii) To validate the obtained model with comparative study.

(iv) To determine the optimum adsorbent condition on acid violet 7 adsorption.

1.4 Scope of Study

In this study, the adsorption of acid violet 7 dye using RHA/CFA sorbent was analyzed and modelled using statistical tools (RSM and ANN), whereby the experimental data was obtained from previous study (Mahdzir, 2018). The relationship between ash ratio, additives concentration and type of additives with the dye removal efficiency were then modelled. Quadratic model was chosen for the modelling, while for the ANN, feedforward backpropagation network was chosen. There are two ANN tools that were being used in this study, which were Matlab ANN toolbox and Wolfram Mathematica. A comparison study was carried out to compare the predicted value from the mathematical model and the experimental data. The fitness of the model is evaluated by statistical parameters such as R^2 and RMSE values. The last part of the study was the optimization. The optimization was performed to obtain the optimum operating conditions in order to achieve maximum adsorption capacity.

1.5 Thesis Overview

This thesis was organized into five chapters including introduction, literature review, materials and methodology, results and discussion, and lastly conclusion and recommendation.

Chapter 1 described the background of the research and problem statements. The objectives of this research were defined, which summarized the aims of this study.

Chapter 2 recorded the literature review to provide related studies in order to have better understandings on current work.

Chapter 3 described the materials and methodology used in this study. Experimental setup for dye adsorption was described, followed by the details of RSM and ANN model development and optimization.

Chapter 4 showed the results and discussion of the research, including analysis of raw data using RSM, performance of model developed, comparison study and optimization of the process.

Lastly, Chapter 5 summarized the results obtained in the study and some recommendations were provided for the reference for future study.

CHAPTER 2

LITERATURE REVIEW

2.1 Dyes and Their Classification

Dyes are used to impart colour to materials. The aromatic structure, also known as chromogen, is required for the resonance which responsible for colour. There are two key components in dye molecules, which are chromophore and auxochrome. Chromophore is the colour giver. Examples of chromophore are –C=C–, –C=N–, –C=O, –N=N– and –NO_2. Normally, the chromophore is coupled with the chromogen. Auxochrome is the bonding affinity group and responsible to enhance the dye solubility in water and affinity towards fibers. Examples of auxochrome are amine, hydroxyl, carboxyl and sulfonic radical. (Malik and Grohmann, 2011;Mahapatra, 2016)

Dyes can be further categorized based on their chemical composition and application. Example of different categories of dye is acid dye, azoic dye, basic dye, direct dye, pigment dye, sulfur dye and vat dye (Mahapatra, 2016;Malik and Grohmann, 2011).The categories of dye and their applications are shown in Table 2.1.

2.2 Acid Violet 7 Dye and Its Treatment

Molecular structure of acid violet (AV 7) dye is shown in Figure 2.1. AV 7 is one of the synthetic dyes that is widely used in food, paper, cosmetic and textile industries. AV 7 is sulfonated azo dye. Azo dyes are organic compound that consist of azo functional groups (-N=N-), which normally bound to aromatic ring. Azo dyes can be broken down into aromatic amines through reductive cleavage and some of the aromatic amines are carcinogenic.

Table 2.1: Industrially important dyes, their classes and applications (Malik and Grohmann, 2011)

Class	Chemical types	Applications
Acid	Azo, anthraquinone, triarylmethane	Nylon, wool ,silk, paper, inks, leather
Azoic	Azo	Cotton, rayon, cellulose acetate, polyester
Basic	Cyanine, azo, azine, triarylmethane, xanthene, acridine, oxazine, anthraquinone	Paper, polyacrylonitrile modified nylon, polyester, inks
Direct	Azo, phthalocyanine, stilbene, oxazine	Cotton, rayon, paper, leather, nylon
Disperse	Azo, anthraquinone, stryl, nitro	Polyester, polyamide, acrylic, and plastics
Natural	Anthraquinone, flavonols, flavones, indigoids, chroman	Food
Pigments	Azo, basic, phthalocyanine, quinacridone, indigoid	Paints, inks, plastics, textiles
Reactive	Azo, anthraquinone, phthalocyanine, formazan, oxazine, basic	Cotton, wool, silk, nylon
Solvent	Azo, triphenylmethane, anthraquinone, phthalocyanine	Plastics, gasoline, varnish, lacquer, stains, inks, fats, oils, waxes
Sulfur	Indeterminate structures	Cotton, rayon
Vat	Anthraquinone (including polycyclic quinones), indigoids	Cotton, rayon, wool

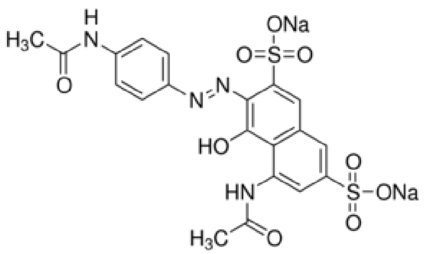

Figure 2.1: Structure of acid violet 7 (Sigma-Aldrich, 2017)

The azo-reduction system of AV 7 by Pseudomonas putida mt-2 under aerobic condition causes reductive cleavage of AV 7 and produces aromatic amines, which are 4'-aminoacetanilide (4'-AA) and 5-acetamido-2-amino1-hydroxy-3,6-naphtalene disulfonic acid (5-ANDS) . The azo-reduction system is shown in Figure 2.2. The toxicity of AV 7 dye increases during the biodegradation process by Pseudomonas putida (Ben Mansour et al., 2010). Ben Mansour et al. (2009) reported that mutagenicity of dyes occurred through free radical generation, such as reactive oxygen species (ROS) formation which responsible for DNA damage. In this case, the presence of the acetanilide group ($NHCOCH_3$) in 4'–AA is the main cause for the formation of ROS. If azo compound is ingested orally, it could be reduced by the gastrointestinal cells in human body and converted to reactive electrophiles and thus form DNA adduct (Alves de Lima et al., 2007). This could be the start of a cancerous cell, where the DNA segment is bound to a cancer-causing chemical.

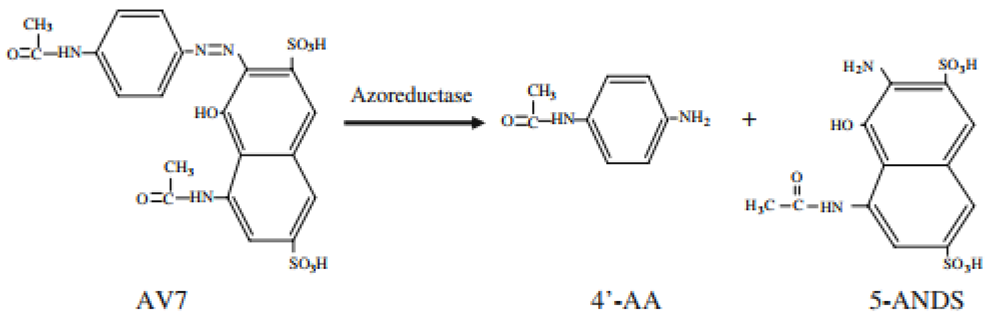

Figure 2.2: Reductive cleavage of acid violet 7 (AV7) by Pseudomonas putida mt-2 (Ben Mansour et al., 2010)

Due to the pollution and health issues caused by AV 7 and other azo dyes present in industrial effluent, the treatment of industrial effluent has become a concern. There are studies on the removal or degradation of AV 7 dye in wastewater such as adsorption, biosorption, biodegradation, advanced oxidation, photocatalytic oxidation, and electrochemical oxidation. Mainly photocatalytic degradation of AV 7 dye was reported using ZnO (Krishnakumar and Swaminathan, 2011), Fe^{3+}-fire clay (Muthuvel et al., 2012) , CdS-SnO_2 (Ghugal et al., 2015), and AgBr-ZnO (Krishnakumar and Swaminathan, 2012) photocatalysts. The methods used in AV 7 treatment is summarized in Table 2.2.

Advanced oxidation process such as Fenton process are suitable to remove both soluble and insoluble dyes. However, the generation of sludge and requirement of UV light hinder the application of advanced oxidation process in wastewater treatment (Robinson et al., 2001;Terangpi and Chakraborty, 2017).

Adsorption is the technique that is widely used in large scale industries due to its low capital, operation costs, high efficiency and simple design (Terangpi and Chakraborty, 2017). Adsorption is one of the physical wastewater treatment method in which the dissolved molecules are attached to the surface of an adsorbent by attractive forces such as Van der Waals forces. There are many kinds of adsorbent that can be used, for example zeolites, charcoal, clays and other waste sources such as coconut shell, rice husk, fly ash, chitosan and many others.

The most widely used adsorbent in industrial wastewater treatment is activated carbon. However, the high cost of activation process limits its utilization in wastewater treatment. The carbon has to be reactivated. Reactivation will result in 10 to 15% loss of the amount of carbon (Martin and Ng, 1984). Hence, industrial waste such as fly ash has been used due to its lower cost.

Table 2.2: Methods used in acid violet 7 treatment

Method used	Categories	Description	References
Photo-catalytic degradation	Chemical method	ZnO is used as photo-catalyst. Optimum dye degradation was found to be 68.2%, with 5×10^{-4} M dye at 2 g/L ZnO catalyst, pH 12.	(Krishnakumar and Swaminathan, 2011)
Photo-catalytic degradation	Chemical method	AgBr-ZnO is used as photo-catalyst. Optimum dye degradation was found to be 94.4%, with 5×10^{-4} M dye at 3 g/L AgBr-ZnO catalyst and pH 12.	(Krishnakumar and Swaminathan, 2012)
Photo-catalytic degradation	Chemical method	CdS-SnO_2 composite is used as photo-catalyst. Complete degradation of dye with 50 mg/L dye, 49CdS-SnO_2 composite by irradiation for 150 min.	(Ghugal et al., 2015)
Photo-catalytic degradation	Chemical method	Fe^{3+}-fire clay (Fe-FC) is used as photo-catalyst. Optimum dye degradation was found to be 77%, with 26% Fe-FC catalyst, with 20 mmol H_2O_2 at pH 7 in solar light.	(Körbahti and Meltem Turan, 2016;Muthuvel et al., 2012)
Electro-Fenton	Chemical method	Glassy carbon meshes electrode as cathode and steel mesh as anode. Removal of total organic carbon (TOC) of the dye solutions is found to be 87% at 70 min.	(Salazar and Ureta-Zañartu, 2012)

Table 2.2: Continued.

Photo electro-Fenton	Chemical method	Glassy carbon mesh electrode as cathode, steel mesh as anode and irradiated with UV radiation. Removal of total organic carbon of the dye solutions is found to be 96% at 70 min.	(Salazar and Ureta-Zañartu, 2012)
Adsorption	Physical method	Chitosan-glutaraldehyde as adsorbent. The optimum pH and contact time for dye removal was found to be pH 4 and 120 mins respectively.	(Hanafiah et al., 2015)

2.3 Statistical Analysis for Adsorption Process

2.3.1 Response Surface Methodology

Response surface methodology (RSM) is a collection of mathematical and statistical techniques for empirical model building. To describe the system studied, linear or square polynomial functions are employed. These functions are then used for modeling the experimental conditions until its optimization.

The stages involved in RSM as an optimization technique are as follows (Bezerra et al., 2008): (1) the selection of factors affect the system through screening studies; (2) the choice of the experimental design and carrying out the experiment; (3)the fitting of a polynomial function based on the experimental data obtained; (4) the evaluation of the model's fitness; (5) the verification of the necessity to perform a displacement in direction to the optimal region; and (6) obtaining the optimum values for each variable.

There are two models that commonly used in RSM, which are:

(i) first degree model

$$y = \beta_0 + \sum_{i=1}^{N} \beta_i x_i + \epsilon \qquad (2.1)$$

(ii) second degree model

$$y = \beta_0 + \sum_{i=1}^{N} \beta_i x_i + \sum_{i<j}\sum \beta_{ij} x_i x_j + \sum_{i=1}^{N} \beta_{ii} {x_i}^2 + \epsilon \qquad (2.2)$$

where N is the number of variables, β_0 is the constant term, β_i is the coefficients of the linear parameters, β_{ij} is the coefficients of the interaction parameters, β_{ii} is the coefficients of the quadratic parameter, x_i is the variables, and ϵ is the residual associated to the experiments. The linear function is shown in Equation 2.1 and the responses should not present any curvature. Second order model represented by Equation 2.2 must be employed to evaluate the curvature.

First order designs are the designs to fit the first degree models. Examples of first order designs are 2^k factorial (k is the number of control variables), Plackett–Burman, and simplex designs. Meanwhile, second order designs are the designs to fit the second order models. Examples of second order designs are 3^k factorial, central composite, and the Box–Behnken designs.

The quality of the model fitted can be evaluated by analysis of variance (ANOVA). By using ANOVA, the variation due to the changes in the combination of variable levels and the variation due to the random errors inherent to the measurements of the generated responses are compared. Sum of square (SS) can be divided into total sum of square (SS_{tot}), sum of square due to regression (SS_{reg}), sum of square due to residual generated by the model (SS_{reg}), sum of square due to pure error (SS_{pe}) and sum of square due to lack of fit (SS_{lof}). Media of square (MS) can be calculated by dividing the sum of square with degree of freedom. Equations related to the source of variations for the calculation of SSs and MSs are also presented in Table 2.3.

2.3.2 Artificial Neural Network

Artificial neural network (ANN) is widely used for prediction, control systems, classification, optimization and decision-making in various fields (Ghaedi and Vafaei, 2017). ANN can model the complex interrelationships between input and output variables, and replace the unknown functional relationships by constructing approximating functions. Type of ANN that is commonly used is the multi-layer perceptron (MLP). MLP consists of one input layer, one output layer and one or more hidden layers. The schematic representation of multilayered ANN is shown in Figure 2.3.

Table 2.3: Analysis of variance for fitted mathematical model to an experimental data set using multiple regressions (Bezerra et al., 2008)

Variation source	Sum of the square	Degree of freedom	Media of the square
Regression	$SS_{reg} = \sum_{i}^{m}\sum_{i}^{n_i}(\hat{y}_i - \bar{y})^2$	$p-1$	$MS_{reg} = \frac{SS_{reg}}{p-1}$
Residual	$SS_{res} = \sum_{i}^{m}\sum_{i}^{n_i}(y_{ij} - \hat{y}_i)^2$	$n-p$	$MS_{res} = \frac{SS_{res}}{n-p}$
Lack of fit	$SS_{lof} = \sum_{i}^{m}\sum_{i}^{n_i}(\hat{y}_i - \bar{y}_i)^2$	$m-p$	$MS_{lof} = \frac{SS_{lof}}{m-p}$
Pure error	$SS_{pe} = \sum_{i}^{m}\sum_{i}^{n_i}(y_{ij} - \bar{y}_i)^2$	$n-m$	$MS_{pe} = \frac{SS_{pe}}{n-m}$
Total	$SS_{tot} = \sum_{i}^{m}\sum_{i}^{n_i}(y_{ij} - \bar{y})^2$	$n-1$	$MS_{tot} = \frac{SS_{tot}}{n-1}$

n_i, number of observations; m, total number of levels in the design; p, number of parameter of model; $\hat{y}_i$, estimated value by the model for the level i; $\bar{y}$, overall media; y_{ij}, replicates performed in each individual levels; $\bar{y}_i$, media of replicates performed in the same set of experimental conditions.

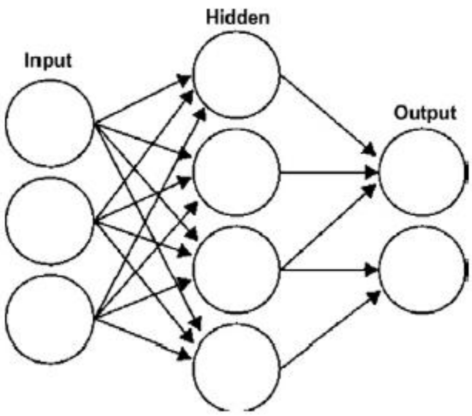

Figure 2.3: Schematic representation of multilayered ANN (Pintér, 2012)

The parameters involved in constructing an ANN model include the network structure, number of parameters, number of hidden layers, number of neurons in each layer, transfer function, training algorithm, momentum factor and training rate. The number of hidden layers, number of neurons, momentum factor and training rate values can be changed to obtain the results with required accuracy.

The neural network is trained using a suitable learning method and a set of matched input-output data. By adjusting the weights and biases, the error between the network output and the actual output can be decreased. The training will stop automatically when the error is within the acceptable value or the maximum epochs are reached. Back-propagation algorithm is a gradient descent algorithm that can be used to learn the multilayer networks with different transfer functions, such as log-sigmoid (logsig), tansigmoid (tansig) and linear (purelin). Normally, logsig transfer function is used for multilayer networks. It produces outputs between 0 and 1 as the node's net input goes from negative to positive infinity. The linear transfer function is normally applied for function fitting problems that show the purelin transfer function. Equations 2.3, 2.4 and 2.5 are the transfer function for logsig, tansig and purelin respectively (Ghaedi and Vafaei, 2017).

$$y = logsig\ (x) = \frac{1}{(1 + \exp(-x))} \tag{2.3}$$

$$y = tansig\ (x) = \frac{2}{(1 + \exp(-2x))} - 1 \tag{2.4}$$

$$y = purelin\ (x) = x \tag{2.5}$$

Before starts the network training, the data have to be normalized between 0.1 to 0.9 by Equation 2.6 to avoid the scaling effect of parameter values (Chowdhury and Das, 2012). x_n is the normalized value of x_i, x_{min} and x_{max} are the maximum and minimum value of x_i respectively. To evaluate the performance of ANN models, values of statistical parameters such as coefficient of determination (R^2), root mean squared error (RMSE) and mean squared error (MSE) are evaluated by altering the model parameters. Value of R^2 implies the fitness of predicted output variable approximation curve to the experimental data output variable curve. A good ANN model has high R^2 and low MSE values. The equations related to the statistical parameters are shown in Equation 2.7, 2.8 and 2.9.

$$x_n = 0.8\left(\frac{x_i - x_{min}}{x_{max} - x_{min}}\right) + 0.1 \quad (2.6)$$

$$MSE = \frac{1}{N}\sum_{i=1}^{N}\left(\left|y_{prd,i} - y_{exp,i}\right|\right)^2 \quad (2.7)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left(\left|y_{prd,i} - y_{exp,i}\right|\right)^2}{\sum_{i=1}^{N}\left(\left|y_{prd,i} - y_m\right|\right)^2} \quad (2.8)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}\left(\left|y_{prd,i} - y_{exp,i}\right|\right)^2}{N}} \quad (2.9)$$

2.3.3 Application of RSM in Adsorption Process

RSM is used to study the adsorption of astrazon red (basic red 46) and sirius blue (direct blue 85) in aqueous solution by sepiolite (Santos and Boaventura, 2008). The factors affect the amount of dye adsorbed including initial dye concentration, initial solution pH and temperature. Box–Behnken design (BBD) was performed to evaluate the relationship between the factors and response. Quadratic models were used to fit the experimental data. The maximum adsorption capacity predicted for astrazon red is 112 mg/g, at C_{in} = 175 mg/L, pH_{in} = 8.0 and T=40 ℃. On the other hand, for Sirius blue, the maximum adsorption capacity was found to be 249 mg/g, at C_{in} = 150 mg/L, pH_{in} = 3.5 and T=30 ℃. The predicted results were acceptable, as from the ANOVA analysis, the R^2 value was closed to 1 for both quadratic model of astrazon red and sirius blue, which were 0.977 and 0.991 respectively.

Singh et al. (2011a) developed a magnetic nanocomposite for the adsorption of crystal violet (CV) dye from water. A four-factor central composite design (CCD) was used to maximize the removal of CV dye. There are four independent variables to be studied, which were temperature (10–50 ℃), pH of solution (2–10), dye concentration (240–400 mg/L), and adsorbent dose (1–5 g/L). The model obtained was used to predict the maximum adsorption of CV dye. The result showed that the maximum dye adsorbed on nanocomposite was 113.31 mg/g under the optimum conditions (concentration 240 mg/l; temperature 50 ℃; pH 8.50; dose 1 g/L). The predicted values were close to the experimental value, which is 111.80 mg/g.

RSM also had been used to study the biosorption of reactive dye (reactive red 198) by waste biomass of Nostoc linckia. The relationship between initial dye concentration, pH and temperature with dye removal was studied. Box-Behnken design was used for modeling the process. Maximum adsorption capacity of the immobilized biomass was 93.5 mg/g at pH 2.0, initial concentration of 100 mg/L and 35 ℃. Good agreement was observed between calculated and experimental values as from the ANOVA analysis, the R^2 value obtained was around 0.997, which is very close to 1.

The papers studied on the application of RSM in modelling dye adsorption were summarized in Table 2.4.

Table 2.4: Application of RSM in modelling dye adsorption

Application	**RSM Design**	**Independent variables**	**Response**	**References**
Adsorption of Astrazon Red (Basic Red 46) and Sirius Blue (Direct Blue 85) by sepiolite	BBD	Initial dye concentration, initial solution pH and temperature	Amount of dye adsorbed	(Santos and Boaventura, 2008)
Adsorption of crystal violet dye from water by magnetic nanocomposite	CCD	Temperature, pH of solution, dye concentration and adsorbent dose	Crystal violet removal	(Singh et al., 2011a)
Reactive dye biosorption by waste biomass of Nostoc linckia	BBD	pH, temperature and initial dye concentration	Dye removal	(Mona et al., 2011)
Bioaccumulation efficiency of Candida utilis for Remazol Turquoise Blue-G (RTBG) dye	CCD	Initial sucrose and RTBG dye concentrations	Growth rate of C. utilis and RTBG dye removal	(Gönen and Aksu, 2009)

2.3.4 Application of ANN Modeling in Adsorption Process

ANN is widely used in modeling of dye adsorption process. Studies on ANN modeling in dye removal process are summarized in Table 2.5. Aber et al. (2007) employed ANN modeling in prediction of time dependency of acid orange 7 removals by powdered activated carbon. Besides contact time, initial dye concentration and initial pH of solution also have effects on the dye removal efficiency. A 3-layer feed forward back-propagation network with 3-2-1 architecture was applied. Transfer function of neurons at first and second layers was tan-sigmoid and at output layer was log-sigmoid. A total of 219 experimental points were randomly split between training and prediction sets with 2:1 ratio respectively. The maximum dye removal efficiency was found to be 96.24% for initial concentration of 150 ppm at pH = 2.8. The model obtained was successfully accepted for predicting the response with mean relative error (MRE) of 5.81%.

Dutta et al. (2010) used ANN to develop an ANN model for adsorption and photo-catalysis of reactive dye on TiO_2 surface. Relationship between pH, amount of TiO2 dose and initial dye concentration with the adsorption efficiency of reactive black 5 was being modeled with feed forward back-propagation network. Different training methods were used, including Levenberg-Marquardt back-propagation algorithm (trainlm), scaled conjugate gradient (trainscg) and resilient back-propagation (trainrp). Among these methods, trainlm gives most satisfactory result, with R = 0.996.

Another study related to the modeling of adsorption of dyes from aqueous solution using rice husk carbon (Khonde and Pandharipande, 2012). A back propagation network with three inputs, two hidden layers with five neurons each and two outputs was used for prediction of concentration of adsorbate in adsorption process. The input factors including the adsorbate coding, initial concentration of adsorbate and adsorbent dosing. The outputs of the study are the equilibrium concentration and % adsorption. The performance of ANN model is evaluated by the RMSE. It was found that the RMSE for the train data is relatively small, which 0.025, while for the test data set the RMSE value was 0.024. The low RMSE value indicates that the ANN model is acceptable and has good prediction toward the responses.

Table 2.5: Application of ANN in modeling dye adsorption

Dye	Adsorbent	ANN characteristics	Input factor	Output factor	Evaluation indices	References
Acid orange 7	Powdered activated carbon	Feed forward back-propagation network with 3-2-1 architecture	Initial dye concentration, time and initial pH of solution	Dye removal efficiency	MRE = 5.81%	(Aber et al., 2007)
Reactive black 5	TiO_2	Feed forward back-propagation network with 3-10-1 architecture	pH,TiO2 dose and initial dye concentration	Adsorption efficiency	R= 0.996	(Dutta et al., 2010)
Bromocresol red, Alizarin red, Malachite green, Methylene blue	Rice husk carbon	Feed forward back-propagation network with 3-5-5-2 architecture	Adsorbate coding, initial concentration of adsorbate and adsorbent dosing	Equilibrium concentration and % adsorption	RMSE(train) = 0.025 RMSE (test) = 0.024	(Khonde and Pandharipande, 2012)

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Overall Study Structure

The overall research activities carried out in this study are presented in Figure 3.1.

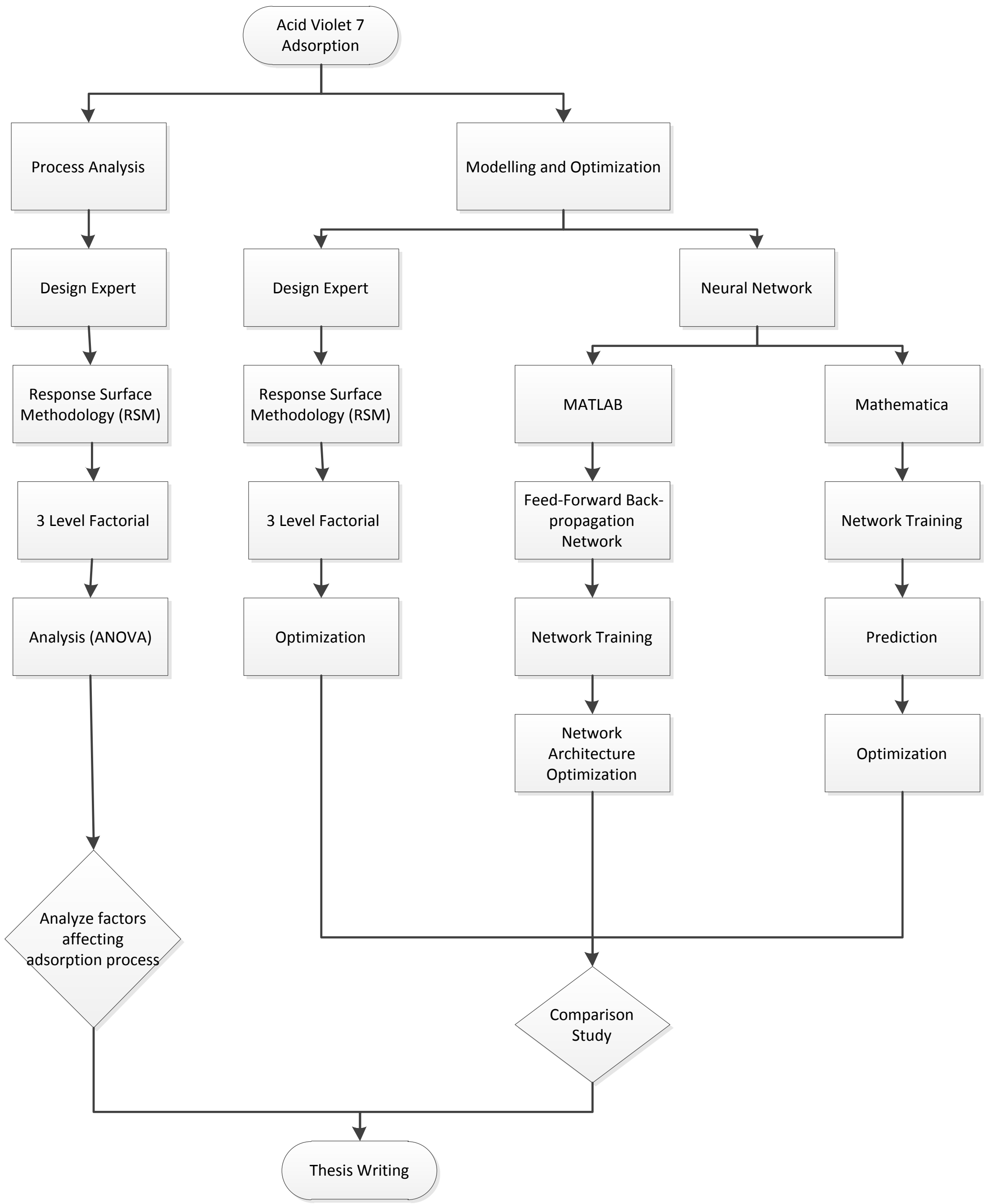

Figure 3.1: Overall research activities

An experiment had been carried out before proceeding to statistical analysis by Mahdzir (2018). The experiment setup and procedures were discussed in Section 3.2, followed by the procedure for statistical analysis in Section 3.3.

3.2 Experimental Procedure

3.2.1 Preparation of Adsorbents and Adsorbate

Adsorbent was prepared through reflux method. Both RHA and CFA were ground separately and sieved through a stack of standard sieves into fine particle size of 75 µm. About 20g of RHA/CFA were mixed with ratio 1:1. The mixture were mixed with 250 mL 1M of additives solution and stirred at 80 ºC for 2 hours. Then, deionized water was used to wash the products until the filtrate become neutral and dried for 110 º C overnight. The additives used were NaOH and Na_2CO_3.

Adsorbate solutions (AV 7) were prepared by dissolving 10g of solid dye into deionized water in 1L volumetric flask, to obtain stock solution with concentration of 10 g/L. Before the adsorption process starts, required amount of stock solution was taken and diluted to obtain desired initial concentration.

3.2.2 Determination of Concentration from Absorbance

The concentration of dye solutions was obtained from the calibration curve. Known concentration of diluted solution ranging from 50 to 300 mg/L were measured using DR 2500 spectrophotometer at wavelength 520 nm. The analytical wavelengths measured were used to plot the calibration curve, with concentration versus absorbance of dye solutions. An equation was obtained from the calibration curve. From the equation, the final concentration of dye solution can be determined.