COMPARISON OF DIFFERENT RSM DESIGNS TO PREDICT AND OPTIMIZE THE ACID VIOLET (AV 7) ADSORPTION USING RHA-CFA ADSORBENT

by

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Project report submitted in partial fulfilment of the requirement for the degree of Bachelor of Chemical Engineering

2021

ACKNOWLEDGEMENTS

This Final year project is for the completion of degree of Bachelor of Chemical Engineering. I would like to show my highest gratitude and appreciation to all the people involved for their contribution throughout my project.

First and foremost, I would like to convey my sincere gratitude to my supervisor, Dr. Irvan Dahlan for his invaluable guidance, insightful supervision, endless encouragement and also his kindness in providing software for the simulation and also listening my problems throughout this project. Without the guidance and advice from him, this final year project will not be done completely on time.

Besides, thank you to my family, fellow friends and course mate for their support and encouragement throughout the time. I would also extend my gratitude to Dean of School of Chemical Engineering, Professor Ir. Dr. Zainal bin Ahmad, my FYP coordinator, Professor Dr. Mohd Roslee bin Othman and all School of Chemical Engineering staffs for their kind cooperation, willing in sharing ideas, knowledge and skills.

One again, I would also like to thank all the people, including those whom I might have missed out who have helped me directly or indirectly in accomplishment of this project. Thank you so much.

Ahmad Aqil Asyraaf bin Mohamad

June 2021

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LIST OF SYMBOLS

A	RHA/CFA ratio	g/g
B	Additive concentration	M
C	Type of additive	-
C_o	Initial Concentration of dye in solution	mg/L
C_e	Final Concentration of dye in solution	mg/L
R^2	Coefficient of determination	-
Y_{NaOH}	AV 7 adsorption efficiency using Naoh as additive	%
Y_{Na2CO3}	AV 7 adsorption efficiency using Na_2CO_3 as additive	%

Greek Letter

α	Distance between center point and star point	-

LIST OF ABBREVIATION

ANOVA	Analysis of variance
AP	Adequate precision
AV 7	Acid Violet 7
CCCD	Central Composite-Circumscribed Design
CCD	Central Composite Design
CCID	Central Composite-Inscribed Design
CFA	Coal Fly Ash
CV	Coefficient of variance (%)
DOD	D-Optimal Design
FCC	Face-Centered Composite design
HDD	Historical Data Design
MSE	Mean Square Error
NaOH	Sodium Hydroxide
Na_2CO_3	Sodium Carbonate
RHA	Risk Hush Ash
RSM	Response Surface Methodology

PERBANDINGAN REKA BENTUK RSM YANG BERBEZA UNTUK MERAMALKAN DAN MENGOPTIMUMKAN PENJERAPAN ASID UNGU (AV 7) MENGGUNAKAN PENJERAP RHA-CFA

ABSTRAK

Dalam kajian ini, faktor-faktor yang mempengaruhi prestasi penjerap Abu Sekam Padi (RHA) Abu Arang Batu (CFA) dalam penyerapan pewarna Asid Ungu 7 (AV7) dianalisis menggunakan pelbagai jenis kaedah permukaan sambutan (RSM). Face-Centered Composite Design, D-Optimal Design dan Historical Data Design dibandingkan berdasarkan nilai R^2, Min Ralat Kuasa Dua (MSE) dan ralat pada bahagian pengoptimuman (%). DOD mempunyai ketepatan tertinggi ($R^2 = 0.9765$) dalam meramalkan kecekapan penjerapan pewarna, sedangkan FCC dan HDD mempunyai ketepatan yang lebih rendah tetapi masih dalam julat nilai yang baik ($R^2 = 0.9335$). Dengan menggunakan perisian Expert Design, keadaan penyediaan adsorben RHA-CFA yang optimum dengan kecekapan penjerapan pewarna AV7 tertinggi diperoleh melalui pengoptimuman berangka model RSM. Pengoptimuman oleh FCC dan HDD, kecekapan penjerapan maksimum yang diperoleh adalah 45.1% dan DOD adalah 44.4% dengan nisbah RHA/CFA 3.00 dan 1.00 M NaOH. Satu eksperimen tambahan nisbah RHA / CFA 3.00 dan 1.00 M NaOH diperoleh dari sastra dan hasilnya digunakan untuk membandingkan dengan nilai yang diramalkan dari setiap reka bentuk RSM. DOD mempunyai ralat terendah pada nilai 2.93% dan kedua-dua model FCC dan HDD adalah 4.43%.

COMPARISON OF DIFFERENT RSM DESIGNS TO PREDICT AND OPTIMIZE THE ACID VIOLET (AV 7) ADSORPTION USING RHA-CFA ADSORBENT

ABSTRACT

In this study, the factors affecting the performance of rice husk ash (RHA)-coal fly ash (CFA) adsorbent in removing acid violet 7 (AV7) dye were analysed using different type of response surface methodology (RSM). Face-Centered Composite Design, D-Optimal Design and Historical Data Design were compared based on the R^2 value, Mean Square Error (MSE) and error in optimization section (%). DOD had the highest accuracy (R^2 = 0.9765) in predicting dye adsorption efficiency, while FCC and HDD have lower accuracy but still in good value range (R^2 = 0.9335). By using Expert Design software, the optimum RHA-CFA adsorbent preparation condition with the highest AV7 dye adsorption efficiency was obtained through the numerical optimization of RSM models. Optimization by FCC and HDD, maximum adsorption efficiency obtained were 45.1% and DOD was 44.4% with RHA/CFA ratio of 3.00 and 1.00 M of NaOH. An additional experiment of RHA/CFA ratio of 3.00 and 1.00 M of NaOH is obtained from the literature and the result from it is used to compare with predicted values of each RSM design. DOD had the lowest error at value of 2.93% and both FCC and HDD models were 4.43%.

CHAPTER 1
INTRODUCTION

1.1 Background

In industry of synthethic dyes production, around 30 million tonnes of dye was estimated for the global consumption for textile industry and expected to grow up by 3% per annum while 70 000 tonnes of dyes were released into the environment (Singh and Arora, 2011). Besides in Malaysia, textile and apparel is one of the fastest growing industries. The textile and apparel are expected to remain as important export products for Malaysia. Exports are targeted to grow at 5.8% from RM13.4 billion in 2010 to RM24 billion in 2020 according to the Ministry of International Trade and Industry. Increasing the growing of textile industry in Malaysia will also increase the usage of textile dyes (MIDA, 2015).

The wastewater from the textile dyeing facilities is difficult to treat because of high composition variability and high colour intensity. It is estimated that about 2% of dyes produced are discharged into effluent while 10% is lost during colourization process in textile industry. The presences of Azo dye in industrial wastewater may create serious environmental problems due to its toxicity behaviour towards aquatic life and mutagenicity to humans (Easton, 1995). Therefore, there are many processes can be done to remove the AV 7 dye such as adsorption, biosorption, biodegradation, advanced oxidation, photocatalytic oxidation and electrochemical oxidation (Dahlan and Ling, 2019). There are advantages and also disadvantages using different method for removal of dye as shown in Table 1.1.

Table 1.1 Advantages and disadvantage of various processes in removing of dye (Tim et al., 2001).

Methods	Advantages	Disadvantages
<u>Chemical treatments</u> **Oxidative process using Fenton's reagent.** **H_2O_2 + Fe(II)**	• Simplicity of application • Fenton's reagent is a suitable chemical means Ozone can be applied in its gaseous state and does not increase the volume of wastewater and sludge	• H_2O_2 agent needs to be activated by some means Sludge generation • Short half-life (20 min)
<u>Photochemical</u> **Sodium Hypochlorite (NaOCl)**	• No sludge is produced and foul odours are greatly reduced initiates and accelerates azo-bond cleavage.	• Formation of by-products • Release of aromatic amines.
<u>Physical treatments</u> **Adsorption by activated carbon**	• Good removal of wide variety of dyes	• Highly cost to purchase the adsorbent.

Adsorption is one of the effective processes of advanced wastewater treatment which industries employ to reduce chemical compound like dye in effluent. Mostly textile industries use commercial activated carbon for removal of dye from the wastewater. Factors affecting dye adsorption such as type of additive, concentration of additive, type of adsorbent used, pH value of solution and also temperature (Singh and Arora, 2011)

Optimization a process means that a selection of the parametric conditions such that the response is maximized or minimized. It is carried out by keeping one factor constant while varying the other factors. This process is called a one factor at a time method. However, this process is a very time-consuming due to the large number of trials involved, along with increased usage of chemicals during the experimental process, thus making it economically expensive. Alternatively, Response surface methodology can be used because it is a method that can take interaction effects into consideration. It consists of a series of mathematical and statistical tools that fit polynomial equations to the experimental data, thus explaining the behaviour of the data set. The goal of RSM design is to optimize many variables simultaneously to achieve optimal performance of the system (Ranade and Thiagarajan, 2017).

In adsorption process modelling, there are number of independent variable that affect the response and also there is also interaction between the independent variables. In order to model this experiment with this variables, Response Surface Methodology (RSM) can be used as an alternative way to use as tool to design adsorption process based experiment and also to optimize the process. RSM usually contains three steps which are design and experiments, response surface modeling through regression and lastly optimization. RSM usage is to determine the optimum operational conditions of the process or to determine a region that satisfies the operating specifications (Myers et al., 2016).

1.2 Problem Statement

As mention before that the presence of dye, such acid violet (AV 7) dye in wastewater can create a serious damage to the environment. This potential hazard need in wastewater need to be treated before being discharge to the environment or to be reused as utility for community. A proper method need to be choose in order to significantly remove the dye such as using adsorption in AV 7 dye removal. In adsorption process, the type of adsorbent RHA-CFA is used and the process is being optimize using RSM design in order to give better performance in adsorption capacity. RSM design include FCC, DOD and HDD. Furthermore, selecting RSM design in predicting and optimizing of a process is important in order to get better results of prediction and optimization perhaps, then is why this study is needed. There is also less study in comparison between the different design models in RSM for adsorption. There is also no study on how to choose which design model is the best to optimize a certain process like adsorption of AV 7 dye using RHA-CFA adsorbent.

1.3 Objectives

In this study, FCC, DOD and HDD are used to predict and optimize the acid violet (AV 7) adsorption using RHA-CFA as its adsorbent. The designs are available in the Design Expert version 6.06 software. The objectives of this project are,

- To compare and predict the Acid Violet 7 adsorption by face-centered composite, d-optimal and historical data designs of RSM.
- To analyse the interaction of independent variable for each model design.
- To optimize the AV 7 adsorption on RHA-CFA adsorbent for every RSM design.

1.4 Scope of Study

The study is focus on modelling and optimizing the Acid Violet 7 adsorption using Central composite, D-optimal and Historical data designs from an existing design matrix data of Three level factorial design. The adsorption of AV7 dye using RHA/CFA as adsorbent and NaOH or Na_2CO_3 as additive. This study analyses the interaction between RHACFA ratio (g/g), additive concentration (M) and NaOH or Na_2CO_3 as additive to the AV7 removal efficiency. The modelling of RSM designs are performed by Design-Expert Software Version 6.06. The results consisted of model design matrix, ANOVA that shows the quadratic equation related to the response surface, the diagnostic plots of predicted value versus actual value, the model graphs and optimization process for every type of RSM designs. The researcher also limited this project on only discussing the value of R^2, MSE and error from the optimization data for every type of RSM designs.

1.5 Thesis Organization

The first part of this chapter is background: water pollution, wastewater treatment, adsorption and RSM designs to design and optimize the AV 7 adsorption. The second chapter, it provides literature review for explaining the term of adsorption, acid violet 7, type of adsorbent and RSM designs. Chapter 3 explains the steps which predicting the best RSM design for the AV 7 adsorption. Chapter 4 discusses the results of model design matrix, ANOVA, model graph and optimization produced by Central composite, D-optimal and Historical data designs. Conclusion and recommendation are in the Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption

Adsorption is the process of purification or bulk separation, depending on the concentration in the feed of the components to be adsorbed (Seader et al., 2010). When it comes to the wastewater treatment, adsorption is also one of promising methods that has been widely studied and applied for removing dyes from industrial wastewater. The advantage of adsorption includes of simple design, environmentally friendly, insensitivity to the toxic pollutants, ability to treat concentrated dye wastes, reusability of the spent adsorbent, high efficiency, and easy to operate (Rai et al., 2015).

When adsorption occurs without any chemical reaction, it is generally termed as physical adsorption "physisorption". It is brought about as a result of Van der Waals forces (Walter and Weber, 1972). These forces are electrostatic in origin, and are termed dispersion forces. Dispersion forces exist in all type of matter and are always present regardless of the nature of other interactions and often account for the major part of the adsorbate–adsorbent potential (Faust and Aly, 1998). Many parameters can affect the quality of physical adsorption; these include properties of the adsorbed material (molecular size, boiling point, molecular mass and polarity) and properties of the surface of the adsorbent (polarity, pore size and spacing) (Cheremisinoff and Cheremisinoff, 1993). Highly functional porous materials (adsorbent) with high surface areas are generally used for such applications as they show excellent efficiency (Okada et al., 2003).

2.2 Acid Violet 7

The use of natural dye for textile dyeing has been practised since the last 5000 years. The discovery of synthetic dyes was stated in 19th century, which has suppressed the use of natural dye. The synthetic dyes such as AV 7 dye can be produced largely and can be utilized in various industries such as fabrics, leather, paper, food, cosmetics, agricultural research, pharmaceuticals, electroplating and distillation (Natarajan et al., 2018).

Due to increase in demand of dyes and development of newer dye molecules, treatment of dye wastewater is becoming serious problem. Dye effluent also create aesthetic problems as they give obnoxious colour to the water (Ahmad and Kumar, 2010). Besides the presence of dyes in water bodies increases chemical oxygen demand and creates hurdle for penetration of light in water bodies affecting photosynthetic of aquatic plant (Sonai et al., 2016).

2.3 Type of adsorbent

Adsorbent is a substance that is used to adsorbs adsorbate that has high selectivity towards adsorbent. With the specific of physical properties, adsorbate will adhere adsorbent's surface when they are in contact. Different adsorbent provides different properties of that affect the adsorption. Three critical properties of adsorbent that determine its suitability and effectiveness of separation of a mixture are selectivity, adsorption capacity and reversibility of adsorption. Furthermore, the characteristics that can also affect the adsorption are particle size and distribution, porosity and pore size distribution, specific surface are, structural strength and stability (Dutta, 2009).

In adsorption of wastewater treatment, choosing adsorbent is important and there are many type of adsorbent can be used. One of the adsorbent can used is activated carbon. The used of activated carbon is perhaps the best broad-spectrum technology available at present. The used of activated carbon in wastewater treatment has increase throughout the world. However, this adsorbent is a costly material, even though it can be regenerated. Therefore, there has been a significant effort in recent years to find cheaper adsorbents such as coal fly ash and rice husk ash to extract dye in wastewater (Astuti et al., 2019).

Now the research is focused on the use of low cost adsorbents derived from the wastes (Senthilkumaar et al., 2011). There are currently numerous treatment processes for effluent discharged from the industrial processes containing dyes, the important and economic method is adsorption process. For example, different type of low-cost, non-conventional adsorbent can be used to adsorb dye are rubber seed coat by Idris et al. (2011), rice husk by Arifur et al. (2012) and cocoa (theobroma cacao) shell by Chinniagounder et al. (2011).

2.3.1 Coal fly ash (CFA)

Coal fly ash (CFA) is a by-product from the combustion of coal used in electric power plants throughout the world. The amount of annually emitted CFA is huge. It has become a trend for removal of dyes using inexpensive adsorbents such as coal fly ash (CFA) (Xie et al., 2014).

CFA is composed of mineral containing some oxides compound such as Al2O3 and SiO2. The existence of active sites in the CFA’s minerals and carbon pores was considered to have roles in the adsorption process with different adsorption mechanisms, namely chemisorption for the minerals and physiorption for unburned carbon. This allows the CFA to become a dual sites adsorbent (Astuti et al., 2019).

2.3.2 Rice husk ash (RHA)

Rice husk is relatively abundant and inexpensive material, is currently being investigated as an adsorbent for removal of various pollutants from water and wastewaters. Various pollution such as dyes, phenols, organic compounds, pesticides, inorganic anions and heavy metals can be removed very effectively with rice husk as adsorbent. The properties of RHA is shown in Table 2.1 below.

Table 2.1 Properties of RHA. (Lataye et al., 2009)

Parameters	**Value**
Average particle size	412 μm
Bulk Density	175.3 kgm^{-3}
Moisture content	1.1%
Volatile matter content	7.36%
Ash content	80.58%
Fixed carbon content	10.96%
Heating value	21.76 $MJkg^{-1}$
BET surface area	65.36 m^2g^{-1}
BJH adsorption surface area of pores	52.35 m^2g^{-1}
BJH desorption surface area of pores	26.62 m^2g^{-1}
Cumulative pore volume	0.039 cm^3g^{-1}
BET pore diameter	34.66 A
BJH adsorption average pore diameter	43.27 A
BJH desorption average pore diameter	58.34 A

These rice husks, as a commodity waste, can also be made into activated carbon, which is used as an adsorbent in wastewater. The used of rice husk as adsorbent also reduce the cost of waste disposal and provide inexpensive alternative to the existing commercially available activated carbons (Mansary and Ghaly, 1998).

2.4 Response surface methodology designs used to design and optimize the experiment

Response surface methodology (RSM) can generate response surfaces and provide optimal solutions for a particular process (Ranade and Thiagarajan 2017). Dahlan and Ling (2019) studied the process of AV 7 dye removal using RHA/CFA as adsorbent, NaOH and Na_2CO_3 as additives. RSM is to be carried out after careful selection of variables that have a major effect on the responses. This can only be done using factorial designs. Factorial designs are the first order designs that estimate the linear functions of the variables on the output. However, these designs can produce curvature results. Second-order designs like Central Composite and Box-Behnken designs can estimate the curvature-interaction of the variable and present it in form of a quadratic equation (Bas and Boyac$_1$, 2007; Bruns et al., 2006; Bazerra et al., 2008). Optimal designs allow user to have an option on choosing the equation whether linear, quadratic or cubic (Ranade and Thiagarajan, 2017).

Optimization is a method used to improve the performance of the system and to increase the yield of the process without increasing the cost. There is a parameter change in the general practice of determining the optimal operating condition while keeping others parameters constant at a certain value, this technique called one-variable-at-a-time. But there is disadvantage of this technique since it does not include interaction among variables. To overcome this issue, RSM is used to conduct the optimization process. RSM is a collection of statistical and mathematical techniques useful for developing, improving and optimizing a process which response influenced by several variables. RSM also important in the design, development of existing product design (Bas and Boyaci, 2007).

A process like adsorption of dye in wastewater, there is a combination of several independent variables and their interaction affect the desired responses, RSM can become an effective tool for optimizing the process (Mason et al., 2003). RSM uses an experimental design such as the Central Composite Design (CCD), D-Optimal and Historical Data to fit a model by least square technique. Adequancy of proposed models is then revealed using diagnostic checking test proved by analysis of variance (ANOVA). The response surface plots can be employed to study the surfaces and locate the optimum (Montgomery et al., 2001).

2.4.1 Central Composite Design

Box and Wilson presented the Central Composite Design in 1951. CCD consists of three types of design-circumscribed, inscribed and faced-centered as shown in Figure 2.1. CCCD involves factorial points, center points as well as star points. Star points represent the extreme values of the variables. The distance between the center point and factorial points is ±1, between center point and star point is α. For CCD, α is greater than 1. For the CCID type, the star points take the specified limit values of the variables. The factorial points lie within the variable limits. The star points and factorial points are located at a distance of ±1 from the center point for the FCC design and therefore, α is equal to 1 (Ranade and Thiagarajan, 2017). While in this experiment, the Face-centered designs is used in order to fit the experiment data provided exactly with the model response surface.

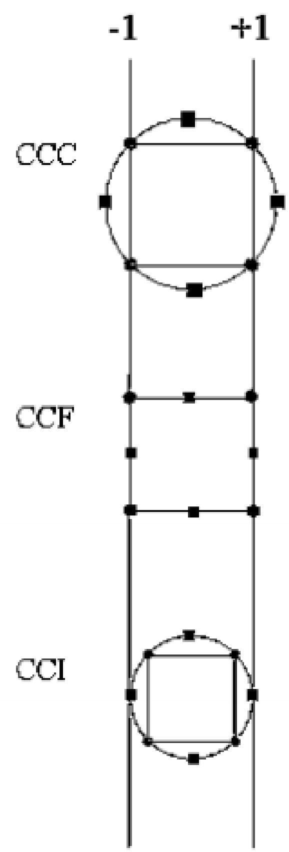


Figure 2.1 Type of central composite designs CCC-Circumscribed, CCF-face-centered and CCI-inscribed (Natrella, 1963).

Central composite designs are used extensively in building second-order response surface models. According to the Bas and Boyaci, 2007, RSM is only usable for the changes which can be described with a second order polynomial equation. Equation 1 shows the example of second model (Montgomery, 2017)

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} {x_1}^2 + \beta_{22} {x_2}^2 + \epsilon \qquad (2.1)$$

2^k central composite design examples are shown in Figure 2.2 below, where k is equal to the number of factor. Central composite design for k=3 factors has 14+n_C runs (Usually 3<n_C<5) and this design is very efficient for fitting the 10-parameter second-order model.

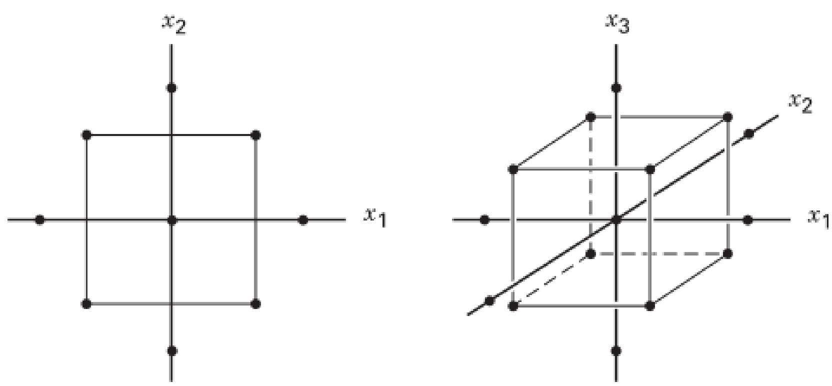


Figure 2.2 (a) Figure 2.2 (b)

Figure 2.2 2^k central composite design examples (a) Two factors and (b) Three factors (Montgomery, 2017)

2.4.2 D-Optimal Design

D-optimal design is generated based on computer algorithms and called computer-aided designs. They are not orthogonal like classic RSM types. The effects of the variables are correlated in these designs. The main advantage here is that it can be used to fit any type of model (first and second orders, quadratic, cubic) or for any particular research objective like screening or generating a response surface. Besides, this optimal designs afford lesser number of experimental trails than classic types and provide a constrained design space. The D stand for determinant. D is an optimality criterion that maximizes the determinant of the information matrix [XX] of the design (Holm et al., 2006; Barot et al., 2012).

There are several popular design optimality criteria, and most widely used is the D-optimal design. A design is said to be D-optimal if $|(X'X)^{-1}|$ is minimized. A D-optimal design minimizes the volume of the joint confidence region on the vector of regression coefficients (Montgomery, 2017).

2.4.3 Historical Data Design

Historical data is used because it can accommodate all available data into blank design layout from an already conducted experiment (Jeirani et al., 2013). It also suitable for conducting multi-factor experiments because it provides information on the influence of factor interactions (Asmara and Ismail, 2013).

For example, the used of Historical Data Design in experiment regarding optimization of sand minimum transport condition (MTC) in pipeline multiphase flow performs by Salam et al. (2018), it revealed the effectiveness of RSM in developing empirical model for prediction of sand MTC in the investigation of sand transport in multiphase pipeline. This model has an advantage because it directly includes the factors under consideration with the aim of studying their interactive effects in contrast to the latter which requires assumptions and experimental determination of factors (Salam et al., 2018).

CHAPTER 3

METHODOLOGY

The flow diagram covered three important key in this studies which are analyzing, modelling and optimizing are shown in Figure 3.1.

Figure 3.1 Flow Diagram of Overall Report

3.1 Experimental design and model development

RSM of Design Expert software version 6.0.6 was used in this study. FCC, DOD and HDDwas used to the model the performance of adsorbent, RHA-CFA in AV7 dye removal by using three factors which are numeric factors includes RHA/CFA ratio and additives concentration and while categorical factors is type of Additives. The data and units of this factors are shown in Table 3.1 below,

Table 3.1 Numeric and Categorical Factors (Dahlan and Ling, 2019).

Factors	Units	Low Actual	High Actual
RHA/CFA ratio	g/g	0.30	3.00
Additives concentration	M	1.00	3.00
Type of additives	-	NaOH	Na_2CO_3

The range of condition for operating parameters are shown in Table 3.1. Adsorption is carried out by 100 mL of 200mg/L AV 7 dye solution was filled into a 250 mL conical flask. RHA-CFA was then added to the dye solution. After shaking and the final concentration of dyes in the solution were measure using DR 2500 spectrophotometer at wavelength 520 nm. The dye removal efficiency can be calculated using the following equation (Dahlan and Ling, 2019).

$$Removal\ efficiency(\%) = \frac{C_O - C_e}{C_O} \times 100 \quad (3.1)$$

Where, C_O(mg/L) is the initial concentration of dye in solution and C_e(mg/L) is the final concentration of dye in solution. Table 3.2 shows the experimental result used in this study.

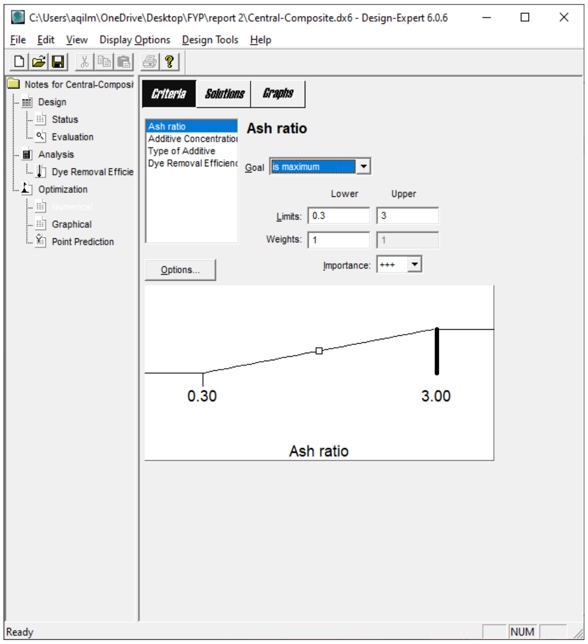
Table 3.2 Experimental Result (Dahlan and Ling, 2019)

Samples	**RHA/CFA Ratio, x_1**	**Additives Conc., x_2**	**Type of Additive**	**AV 7 Adsorption (%)**
S1	0.30	1	NaOH	17.59
S2	1.65	1	NaOH	36.69
S3	3.00	1	NaOH	41.87
S4	0.30	2	NaOH	13.21
S5	1.65	2	NaOH	39.29
S6	3.00	2	NaOH	54.68
S7	0.30	3	NaOH	14.51
S8	1.65	3	NaOH	48.39
S9	3.00	3	NaOH	64.46
S10	1.65	2	NaOH	44.86
S11	1.65	2	NaOH	46.38
S12	1.65	2	NaOH	41.15
S13	1.65	2	NaOH	40.1
S14	0.30	1	Na_2CO_3	15.53
S15	1.65	1	Na_2CO_3	30.7
S16	3.00	1	Na_2CO_3	33.34
S17	0.30	2	Na_2CO_3	20.63
S18	1.65	2	Na_2CO_3	36.92
S19	3.00	2	Na_2CO_3	33.32
S20	0.30	3	Na_2CO_3	13.18
S21	1.65	3	Na_2CO_3	32.02
S22	3.00	3	Na_2CO_3	43.28
S23	1.65	2	Na_2CO_3	34.74
S24	1.65	2	Na_2CO_3	25.93
S25	1.65	2	Na_2CO_3	25.81
S26	1.65	2	Na_2CO_3	23.84

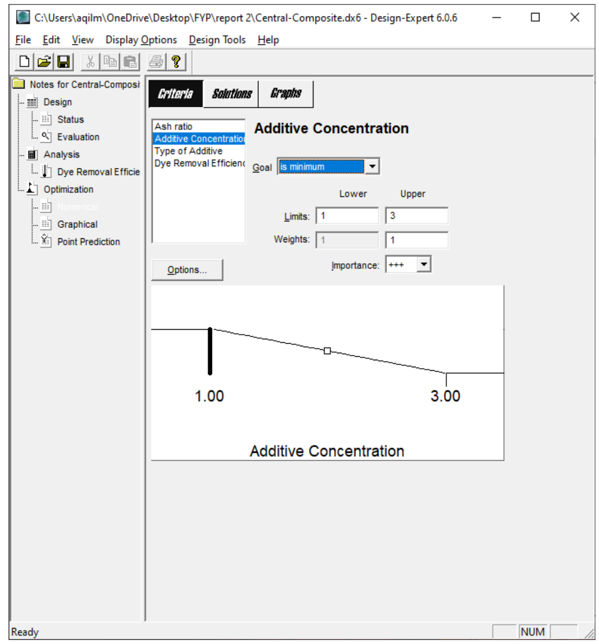
After fitting the model design matrix from the Table 3.2 into Central Composite, D-Optimal and Historical Data Designs, ANOVA is generated and being analysed. The R^2 value and MSE represent the performance of the RSM design and its performance can be seen in predicted value versus actual value plot. From ANOVA, the final regression model as a function of RHA/CFA ratio (A), additive concentration (B) and types of additive (C) can be generate in form of quadratic equation and this equation is used to plot model graph for every RSM design. Interaction of factor involved can be clearly seen as the model graph in 3D view is plot for every RSM design.

3.2 Optimization of acid violet 7 adsorption and comparison between design models.

Using the Design Expert software, the values of RHA/CFA ratio is maximized, additive concentration is minimized and the type of additive can be determined at which the adsorption capacity was at maximum. To maximize the result of AV7 removal efficiency according to desire optimum condition, the following steps were taken prior to identify the criteria of the numerical optimization. First, the goal factors for the RHA/CFA ratio is set to “is maximum”, additive concentration is set to “is minimum” and type of additive were set to “is equal to > NaOH” as shown in Figure 3.2 (a)(b)(c), then AV7 removal efficiency was set to “maximum” as shown in Figure 3.2 (d). Then, the step was repeated for all three models which are d-optimal, central-composite and historical data designs.



(a)



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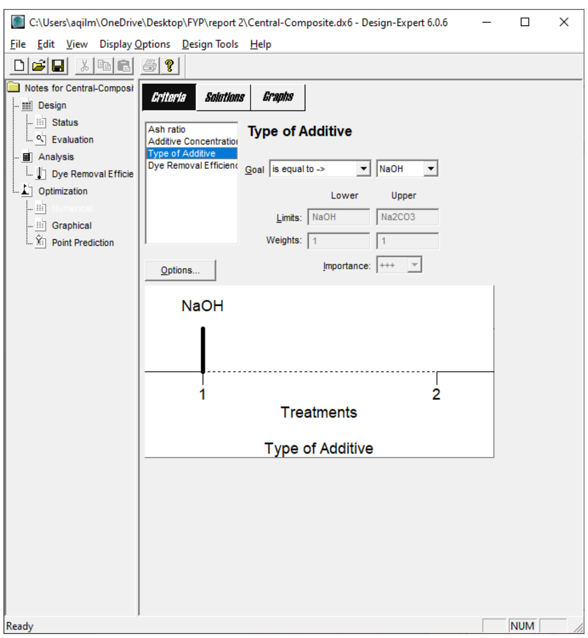
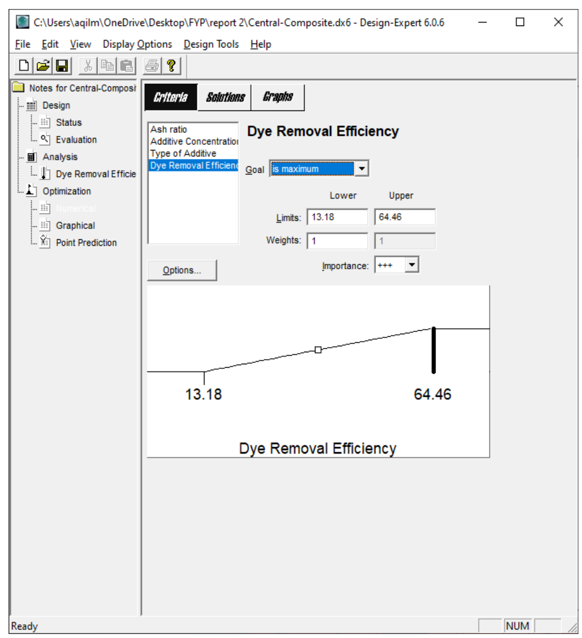


(c)



(d)

Figure 3.2 Optimization criteria on (a) RHA/CFA ratio and (b) Additive concentration (c) Type of additive and (d) Dye removal efficiency.

These criteria are used because RHA/CFA as adsorbent is inexpensive so it need to be set to maximize in its usage. While the usage of additive NaOH and Na_2CO_3 is quite expensive and need to limit it. The NaOH yields higher dye removal efficiency than Na_2CO_3. Besides these criteria/optimum condition for the adsorption need to be used as mentioned earlier because an additional experiment need to be carried out in order to compare the experimental value (taken from Dahlan and Ling (2019)) with the value produced by the different design.

CHAPTER 4

RESULTS AND DISCUSSIONS

This chapter presents the results obtained from the work as described in Chapter 3. All the data and results are thoroughly discussed to meet the outlined research objectives.

4.1 Model Design Matrix and ANOVA

4.1.1 Face-Centered Composite Design

The complete design matrix and results of FCC (with α=1) for AV 7 dye adsorption by RHA-CFA adsorbent is exactly follow the data shown in Table 3.2. The efficiency of the AV 7 adsorption varied between 13.2 % and 64.5 %. The AV7 adsorption efficiency was moderate (ranging from 13.21% to 64.46%) for additive NaOH at the central point (with RHA/CFA ratio of 1.65 and 2.00 M of NaOH or Na_2CO_3) repetition run from S9 to S13. On the other hand, the use of Na_2CO_3 as an additive (experiment run S22 to S26) resulted in slightly lower AV7 adsorption efficiency (ranging from 13.18% to 43.28%) as compared to NaOH. This result suggested that the optimum condition for AV7 adsorption system did not occur in the central point. Overall, the highest dye removal efficiency was observed at run S4, which was 64.46%, with RHA/CFA ratio of 3.00 and 3.00 M of NaOH as additive. On the other hand, the lowest dye removal efficiency was observed at run S16, which only removed 13.18% of dye, with RHA/CFA ratio of 0.300 and 3.00 M of Na2CO3 as additive. According to the experimental results, better performance of dye removal required high ash ratio and high concentration of additive.

Using multiple regression analysis, the response (experimental AV7 adsorption removal efficiency) obtained in Table 3.2 was correlated with the three adsorbent preparation variables using the mathematical model as shown in Eq. (1). The final regression model as a function of RHA/CFA ratio (A), additive concentration (B) and types of additive (C) is given as follow

$$Y = 36.5 + 14.69\text{A} + 3.34\text{B} - 5.15\text{C} - 5.94A^2 + 0.55B^2$$

$$+4.75AB - 4.59AC - 1.89BC \qquad (4.1)$$

Whereas the AV7 adsorption efficiency based on the categorical factor (types of additive) was expressed in Equations 4.2 and 4.3, respectively.

$$Y_{NaOH} = 12.13336 + 18.01550\text{A} - 2.78536\text{B} - 3.26096A^2 + 0.54690B^2$$

$$+3.51481AB \qquad (4.2)$$

$$Y_{Na_2CO_3} = 20.48770 + 11.21303\text{A} - 6.50203\text{B} - 3.26096A^2 + 0.54690B^2$$

$$+3.51481AB \qquad (4.3)$$

Statistical analysis was performed by ANOVA to analyse the model. The statistical parameters obtained for central composite design are tabulated in Table 4.1. ANOVA results were calculated based on 95% confidence level. F-statistic and lack of fit tests were used to evaluate the regression model. Based on Table 4.1, F-value of 29.84 indicated that the model was significant. The quadratic model with “Prob>F” less than 0.0500 indicates the model had a significant effect on the response. In this case, A, B, C, A^2, AB, AC and BC were significant model terms. Besides, lack of fit test with “Prob>F” value greater than 0.0500 proved that the model had satisfactory fitness to the actual data shown in B^2 which has value of 0.7603.

Table 4.1. ANOVA for the regression model equation and coefficients for FCC

Source	**Sum of squares**	**DF**	**Mean square**	**F value**	**Prob>F**	
Model	4.10×10^3	8	512.87	29.84	<0.0001	Significant
A	2590.14	1	2590.14	150.71	<0.0001	
B	134.13	1	134.13	7.80	0.0125	
C	690.00	1	690.00	40.15	<0.0001	
A^2	195.10	1	195.10	11.35	0.0036	
B^2	1.65	1	1.65	0.096	0.7603	
AB	180.12	1	180.12	10.48	0.0048	
AC	253.00	1	253.00	14.72	0.0013	
BC	41.44	1	41.44	2.41	0.1389	
Residual	2.9×10^2	17	17.19			
Lack of Fit	112.86	9	12.54	0.56	0.7977	Not significant
Pure Error	179.30	8	22.41			
Cor Total	4.4×10^3	25				
R^2		0.9335				
Adjusted R^2		0.9022				
Predicted R^2		0.8459				
Adequate precision, AP		21.686				
Coefficient of variance, CV (%)		12.35				

The standard R^2 value for a good model is 0.8 (Hosmer and Lemeshow, 2004). FCC's R^2 value was found at 0.9335. This value shows that only 6.65% of the variation the response cannot be explained by the model and it also shown that this model is good to use in this experiment. Adequate precision (AP) measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The AP value obtained for the quadratic model was 21.686, indicating there had adequate signal and the model can be used to navigate the design space. Coefficient of variance (CV) is the standard deviation expressed as a percentage of the mean. CV is an important measure of experimental precision. Lower CV value indicates a higher precision of the experiment for a determined parameter (Faria et al., 2010).

The CV value obtained from ANOVA analysis was slightly lower, which was only 12.35%. This result suggested that the adsorption system was well controlled and had high accuracy.

4.1.2 D-Optimal Design

The complete design matrix and results of d-optimal design for AV 7 dye adsorption by RHA-CFA adsorbent is exactly same following the data shown in Table 3.2. The central point provided from the d-optimal design is only 2 which at S3 and S18. At S3, the AV 7 removal efficiency was 39.29% using NaOH as additive and at S18 the AV 7 removal efficiency was 25.81% using Na_2CO_3 as additive.

The final regression model as a function of RHA/CFA ratio (A), additive concentration (B) and types of additive (C) for d-optimal design model is given as follow