STATISTICAL MODELING AND OPTIMIZATION OF PROCESS PARAMETERS FOR 2,4-DICHLOROPHENOXYACETIC ACID REMOVAL BY USING AC/PDMAEMA HYDROGEL ADSORBENT: COMPARISON OF DIFFERENT RSM DESIGNS AND ANN TRAINING METHODS

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by

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LIST OF SYMBOLS

Symbol	Description	Unit
α_i	Overall Value of Mean	-
α	Coded Distance in FCCD	-
β_0	Coefficient for Intercept	-
β_i,	Coefficient for Linear	-
β_{ii}	Coefficient for Quadratic	-
β_{ij}	Coefficient for Interaction Parameters	-
β_i	Effect of Factors to Output of the Process	-
C_I	Initial Concentration	mg/L
C_E	Final Concentration	mg/L
C.V	Coefficient of Variation	%
ε	Residual Associated to the Experiments	-
ε_i	Residual Error	-
k	Number of Factor	-
M	Mass of Dry Adsorbent	g
N	Number of Experiment or Number of Data	-
n_c	Number of Centre Point	-
p	Level of Factor	-
R	Coefficient of Correlation	-
R^2	Coefficient of Determination	-
2k	Star or Axial Point	-
V	Volume	mL
x_i	Experimental or Input Factor	-

x_n	Normalized Experimental Factor	-
x_{min}	Minimum Value of Experimental Factor	-
x_{max}	Maximum Value of Experimental Factor	-
y_n	Normalized Experimental Response	-
$\hat{y}$	Predicted Response or Output	-
Y_i or y_i	Measure Value or Experimental Result	-
$y_{prd,\ i}$	i^{th} Predicted Response	-
$y_{exp,i}$	i^{th} Experimental or Measured Value	-
y_m	Mean Value of Measured Value	-

LIST OF ABBREVIATION

2FI	Two Factor Interaction Model
2,4-D	2,4-Dichlorophenoxyacetic Acid
AC	Activated Carbon
ANN	Artificial Neural Network
ANOVA	Analysis of Variance
APS	Ammonium Persulfate
BBD	Box–Behnken Design
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
CCD	Central Composite Design
CCCD	Circumscribed Central Composite Design
DMA	Dimethylamino
DO	Dissolved Oxygen
DOE	Design of Experiment
FCCD	Face Centred Composite Design
FFD	Full Factorial Design
FOR	Ferrioxalate-exchanged Resin
FR	Ferric-Exchange Resin
GAC	Granular Activated Carbon
H_2O_2	Hydrogen Peroxide
HRT	Hydraulic Retention Time
ICCD	Inscribed Central Composite Design
LPS	Lacto Peroxidase System

MBAM	Methylenebiscryllamide
MSE	Mean Squared Error
MI	Molecular Imprinting
NaSCN	Sodium Thiocyanate
OVAT	One Variable at a Time
O_3	Ozone
PDMAEMA	Poly (Dimethylaminoethyl methacrylate)
PI	Prediction Interval
Pt	Platinum
PVC	Polyvinylclorua
RMSE	Root Mean Square Error
RSM	Response Surface Methodology
RSS	Residual Sum of Square
Sb	Antimony
SBR	Sequential Bed Reactor
SnO_2	Tin Oxide
TBC	Total Bacteria Count
TCC	Total Coliform Count
TOC	Total Organic Content
TiO_2	Titanium Oxide
UV	Ultraviolet
WHO	World Health Organization

PEMODELAN STATISTIK DAN PENGOPTIMUMAN PARAMETER PROSES UNTUK PENYINGKIRAN ASID 2,4-DIKLOROFENOKSIASETIK DENGAN MENGGUNAKAN PENJERAP AC/PDMAEMA HIDROGEL: PERBANDINGAN REKA BENTUK RSM DAN KAEDAH LATIHAN ANN YANG BERBEZA

ABSTRAK

Kesan pH, kepekatan awal 2,4-D dan kandungan karbon teraktif terhadap proses penjerapan 2,4-D oleh hidrogel diubah suai (hidrogel AC/PDMAEMA) telah dianalisis. Data eksperimen yang diambil daripada kajian lepas digunakan untuk meramalkan penyingkiran 2,4-D dan kapasiti penjerapan. Simulasi telah dilakukan dengan Pakar Reka Bentuk V12.0 dan Matlab R2021a, di mana reka bentuk kaedah permukaan tindak balas (RSM) yang berbeza dan kaedah latihan Rangkaian Neural Tiruan (ANN) telah digunakan. RSM digunakan untuk menganalisis kesan parameter proses terhadap proses penjerapan 2,4-D serta membina model empirikal yang memaparkan hubungan antara faktor dan tindak balas. Analisis binaan model empirikal oleh dua peringkat faktorial, komposit berpusat muka dan reka bentuk tersuai telah dilakukan dengan analisis varians (ANOVA) dan dibandingkan. Selain daripada prestasi model empirikal, keadaan optimum untuk penyingkiran maksimum 2, 4-D dan kapasiti penjerapan juga diperoleh dengan simulasi RSM. Didapati bahawa antara ketiga-tiga reka bentuk ini, reka bentuk optimum mempunyai ketepatan yang paling tinggi dalam meramalkan tindak balas. Penyingkiran maksimum 2, 4-D dan kapasiti penjerapan masing-masing pada 65.01 % dan 65.29 mg/g diperoleh pada pH 3, kepekatan awal 2,4-D sebanyak 94.52 mg/L dan 2.5 wt% karbon teraktif. Selain daripada pengoptimuman parameter proses, seni bina rangkaian saraf juga telah dioptimumkan melalui percubaan dan ralat dengan bilangan neuron tersembunyi yang berbeza dalam lapisan untuk mendapatkan prestasi terbaik bagi tindak balas. Pengoptimuman

rangkaian saraf dilakukan dengan kaedah latihan yang berbeza dan dibandingkan. Didapati bahawa antara tiga kaedah latihan model ANN, kaedah Regularisasi Bayesian mempunyai R^2 tertinggi dan MSE terendah dengan seni bina rangkaian optimum 3:9:2. Keadaan optimum yang diperoleh daripada RSM juga telah disimulasikan dengan seni bina rangkaian neural yang dioptimumkan untuk mengesahkan tindak balas dan kecukupan model RSM.

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ABSTRACT

The effect of pH, initial concentration of 2,4-D and the activated carbon content toward the adsorption process of 2,4-D by the modified hydrogel (AC/PDMAEMA hydrogel) were analysed. The experimental data taken from previous study was used to predict the removal of 2,4-D and the adsorption capacity. The simulation was done with Design Expert V12.0 and Matlab R2021a, where different design of response surface methodology (RSM) and training methods of Artificial Neural Network (ANN) were used. RSM was used to analyse the effect of the process parameter toward the adsorption process of 2,4-D as well as to build an empirical model which display the relationship between the factors and the responses. The analysis of the empirical model build by the two level factorial, face centred composite and custom designs were done with the analysis of variance (ANOVA) and compared. Apart from performance of empirical model, the optimum condition for the maximum removal of 2, 4-D and adsorption capacity was also obtained with the RSM simulation. It was found that among these three design, the optimal design has the highest accuracy in predicting the responses. The maximum removal of 2, 4-D and adsorption capacity at 65.01 % and 65.29 mg/g respectively were obtained at pH of 3, initial concentration of 2,4-D of 94.52 mg/L and 2.5 wt% of activated carbon. Apart from optimization of process parameter, the neural network architecture was also optimized by trial and error with different number of hidden neurons in the layers to obtain the best performance of the response. The optimization of the neural network was done with

different training methods and compared. It was found that among the three training methods of ANN model, Bayesian Regularization methods had the highest R^2 and lowest MSE with optimum network architecture of 3:9:2. The optimum condition obtained from RSM was also simulated with the optimized neural network architecture to validate the responses and adequacy of the RSM model.

CHAPTER 1
INTRODUCTION

1.1 Research Background

Water is one of the most vital resources in the world due to their variety of usage in both domestic and industrial application. Among these, agriculture is found to contribute about 70% usage of surface water supplies (Food and Agriculture Organization of the United Nations, 2005). The wide usage of pesticides in agriculture for pest control led to water pollution. 2,4-dichlorophenoxyacetic acid (2,4-D), one of the most commonly used herbicides due to its low cost and higher selectivity is the major cause for these pollution. The carcinogenic and mutagenic effect of this herbicide are harmful to both the human and aquatic life (Aziz et al., 2018). Therefore, the world health organization (WHO) provided a guideline for the maximum allowable concentration of contaminant in the wastewater before being discharged into the water bodies. The specific standard concentration of 2,4-D in the drinking water recommended by the world health organization (WHO) is 20 μg/L (Mir et al., 2020). For the removal of these pollutant from wastewater, the adsorption process is found to be the most economical in the wastewater treatment apart from their high flexibility in the design and operation (Bazrafshan et al., 2013).

Design of the experiment (DOE) is the systematic approach or method which is used to determine the relationship between factors and response in the process (Montgomery, 2008). The conventional approach for DOE includes one variable at time (OVAT), where this method require a lot of time (Prabhu et al., 2015). In addition, the cost to conduct the study using this method is quite high as many tests and runs need to be conducted (Witek-Krowiak et al., 2014). Recently, there are more sophisticated method and statistical software packages that can be used to perform these design of experiment (Nair et al., 2013). Design Expert software is one of them. In this software, there are many classes of design of response surface methodology (RSM) can

be generated, for example Central Composite Design (CCD), Box-Behnken Design (BBD) etc. These different design available in the software able to perform various statistical analysis like building a mathematical model that fit the experimental data as well as optimizing the output of the experiment if needed (Montgomery et al., 2008).

The response surface method (RSM) is considered as one of the best technique for the design of experiment, where it is useful in optimizing the response apart from analyzing the problem where the independent variable is affecting the dependent variable (Mourabet et al., 2014). The dependent variable, in this case is the output or response of the experiment while the independent variable is the factor or input of the process. For optimization of the response, RSM is typically used to select the operating condition that fits the user requirement or specification (Maran et al., 2013). For instance, by selecting highest output response as the target of the process, the user is able to obtain the optimum condition for the input to achieve the required responses.

Apart from that, Artificial Neural Network (ANN) also has risen recently due to its efficient and attractive approach for the modeling of nonlinear multi factor (Aklilu et al., 2021; Yang et al., 2015). ANN is a computational model which simulates the structure and functionalities of biological neural networks. Since ANN is able to simulate complicated system more efficiently as it do not require mathematical description of phenomena in the process, the modeling and simulation of real process is suitable using ANN. Indeed, it has already been utilized in many applications like food science and biochemical. It also has been used in the real engineering applications like food engineering for modelling and prediction of mass transfer coefficient during osmotic dehydration of Carica Papaya (Maran et al., 2013).

Taktak et al. (2015) found that adsorption process by using activated carbon from pomegranate husk introduced into the poly((2-dimethylamino) ethyl methacrylate) network to form composite hydrogel (named as AC/PDMAEMA hydrogel) has great improvement in the

mechanical and physical properties as well as the cost and adsorption capacity. However, instead of the conventional OVAT, the RSM method with Face Centered Composite Design (FCCD) is used in their study. Recently, many researchers have found that ANN has higher prediction ability than RSM. Therefore, the selection of the model and appropriate design or training method are important to ensure the optimum condition for the desired response is obtained.

1.2 Problem Statement

Recently, water pollution has become one of the most popular issues in the world. This type of pollution is mainly contributed by the herbicide or pesticide used by the farmer in the agriculture (Food and Agriculture Organization of the United Nations, 2005). 2,4-D is one of the major causes for the pollution since it is being widely utilized due to its cheaper price (United States Environmental Protection Agency, 2015; Taktak et al., 2015). It is found that adsorption process is the commonly used method for removal of 2,4-D from the wastewater because it is very simple and cheap (Bazrafshan et al., 2013). In addition, the usage of modified hydrogel as the adsorbent has greatly improved the adsorption efficiency and overcome the problem with high cost of activated carbon (Taktak et al., 2015; Tran et al., 2018).

However, the performance of the process may vary with different methods used in their design of experiment (DOE). The conventional method, one variable at time (OVAT) require a lot of time as large number of experiments is needed to screen all variable independently (Witek-Krowiak et al., 2014). Consequently, high cost is needed to conduct the study due to high number of test and runs needed. Thus, multivariate statistics technique such as RSM and ANN which offer lower cost, number of experiments and also the description for interaction between the independent variable are more preferred for adsorption of 2,4-D. Nevertheless, there are less study on comparison between different RSM designs and ANN training methods.

The modelling and optimization of the process with different designs and training methods in RSM and ANN respectively could offer variety of performance in term of optimum condition for the process and prediction capability. Selecting RSM design is important to get better prediction and optimum result as there are many different designs in RSM. On top of that, selection of architecture in the neural network especially the number of hidden layer or nodes could affect the performance of the process (Zhang et al., 1998). The optimum method for selection of these nodes has yet to be found as usually they are based on the trial and error coupled with empirical result for minimization of the error (Witek-Krowiak et al., 2014). Since 2,4-D have carcinogenic and mutagenic effect to human, it is important to ensure the optimum condition that can maximize the performance of the adsorption process by considering the right method for the DOE.

1.3 Objectives

i. To predict and optimize the 2,4-D removal by modified hydrogel (AC/PDMAEMA hydrogel) using different RSM design and ANN training method.

ii. To analyse the interaction of independent variable toward the responses.

1.4 Scope of Study

In this study, the simulation for adsorption process for removal of 2,4-D using modified hydrogel (AC/PDMAEMA hydrogel) was conducted with different designs of RSM and ANN training methods . The data for the simulation was taken from previous study by Taktak et al. (2015). In the simulation, Design Expert V12.0 and Matlab R2021a were used for both modeling and optimization of the process as well to analyze the interaction between the independent variables. At the end of study, the interaction between the process factors with the response and the performance of the process with respect to the two statistical tools used were being compared and analyzed.

CHAPTER 2

LITERATURE REVIEW

2.1 Water Pollution and Type of Pollutant

Fresh water is essential to maintain the environment and life of living things in the world, be it human, animal or plant. River, lake and pond are example of resources for water. The increase in population has led to scarcity of fresh water due to urbanization and industrialization. This is because the amount of both domestic waste and industrial waste which contribute to pollution of water bodies will increase with emerging of new industries and households. Nevertheless, the type and composition of pollutant may differ according to source of pollution to the water bodies (Saravanan et al., 2021). Table 2.1 summarize the type of pollutants available from different sources with their respective effect to human and environment.

Among all the sources of pollution listed in Table 2.1, agriculture practices which contribute about 70% usage of surface water supplies are one of the major causes of water pollution (Food and Agriculture Organization of the United Nations, 2005). It is expected that the production of food crops to increase about 53% by 2050, correspond to an increase of 4.23 billion tons compared to 2015 (Porter, 2016; Karic et al., 2022). This is to meet the increasing demand for the supply of food as the population of human keeps growing by years.

Pesticides and herbicides are example of pollutant commonly found in the wastewater from or near the agriculture area. The usage of these chemicals is important to kill or control the pest and manipulate undesired vegetation of crops respectively (United States Environmental Protection Agency, 2015). Although these chemicals are detrimental to human society and environment due to its carcinogenic and mutagenic effect, it is still used till today. The reason is these chemicals could offer many benefits to the agriculture industries according to the different type of herbicides or pesticides used.

Table 2.1: Summary of different type of pollutants available from different sources with their respective effect to human and environment (Saravanan et al., 2021)

Type of Pollutants	Sources of Pollution	Effects of pollutants	
		Human	Environment
Heavy metals	Sewage sludge, mining, pesticides and industrial discharge	Carcinogenic, organ disability	Bioaccumulation and oxidative stress in plants
Dyes	Industrial discharge from textile , paint and paper industries	Carcinogenic, mutagenic, organ impairment	Reduce the photosynthesis of plant, increase the level of biological oxygen demand (BOD) and chemical oxygen demand (COD), retard the growth of plants
Oil	Oil spillage, Industrial discharge	Respiratory or breathing diseases, carcinogenic diseases, irritation of eye and noses	Destruction of aquatic habitat, decrease in the amount of dissolved oxygen (DO) in water
Plastics	Disposal of non-degradable plastic or packaging material	Damage of liver and immune system, hearing and lung problem	Blockage of respiration system of aquatic animals and plants
Pesticides and Herbicides	Agriculture practices	Impairment of organ, disrupt the endocrine system	Biomagnification, reduce the biodiversity

2.2 2,4-Dichlorophenoxyacetic acid (2,4-D)

2,4-Dichlorophenoxyacetic acid (2,4-D) could be classified as phenoxy herbicide with molecular formula of $C_8H_6Cl_2O_3$ and structural formula as shown in Figure 2.1 (Bazrafshan et al., 2013). It is widely used for control of broad-leaved weeds in the cereal cropland, forest, pastures and even in the area adjacent to water (Aziz et al., 2018). On top of that, it is also being used as growth regulators for the plants whereby it could inhibit the growth of broad-leaved plant once it translocated and accumulated within the plants. (United States Environmental Protection Agency, 2015; Bazrafshan et al., 2013).

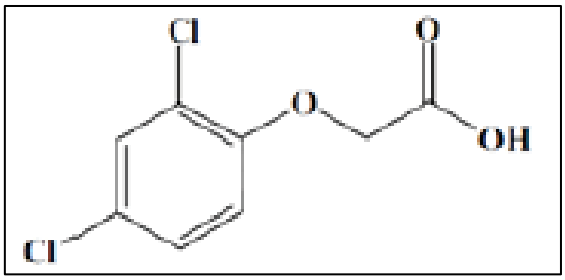

Figure 2.1: Structure of 2,4-D (Bazrafshan et al., 2013)

Figure 2.2 shows the application of different type of herbicides per millions of acres land for agricultures where it can be seen that 2,4-Dichlorophenoxyacetic acid (2,4-D) can be categorized as one of the most used herbicides in agriculture besides Atrazine and Glyphosate.

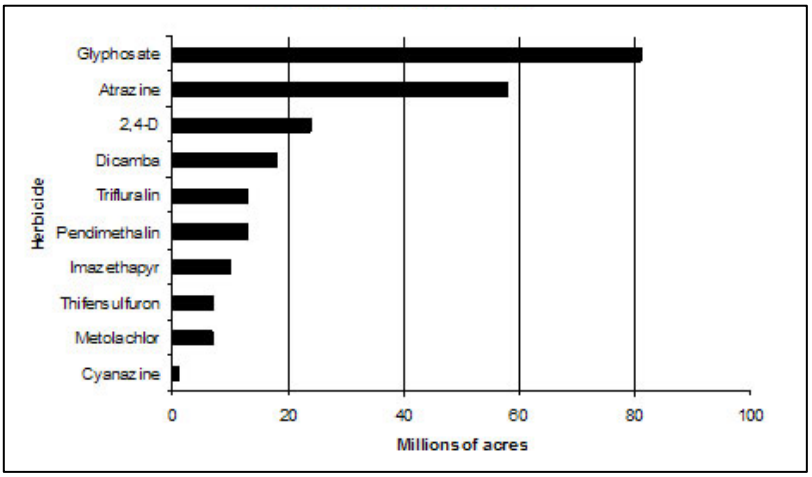

Figure 2.2: Herbicides applications per millions of acres land for agricultures (United States Environmental Protection Agency, 2015).

The widespread use of this herbicide is because of its low cost of application and selective control of many broadleaf weeds (Taktak et al., 2015; Marcinkowska et al., 2017). Its residue is often found in the surface and the ground water due to their high potential of leach ability, low sorption of soil and poor biodegradability (Shankar et al., 2006; Aksu and Kabasakal, 2004). The half life of this herbicide in the water could differ based on the amount of oxygen present in the water. Under aerobic condition, its half life is between one to several weeks and it could be more than 120 days under anaerobic conditions (Bazrafshan et al., 2013).

The International Agency for Research on Cancer has classified 2,4-D as very toxic due to its possible carcinogen and mutagen impact to human (Mir et al., 2020). This is because 2,4-D could disrupt both endocrine and central nervous system of human (Bradberry et al. 2004). On top of that, it could cause moderate and severe irritation to skin if being exposed for a long duration (Njoku and Hameed, 2011). Therefore, the World Health Organization (WHO) have provided a guideline for the maximum allowable concentration of contaminant in the wastewater before being discharged into the water bodies. The specific standard concentration of 2,4-D in the drinking water recommended by WHO is 20µg/L (Mir et al., 2020).

2.3 Wastewater treatment for 2,4-D removal

Due to the harmful effects of 2,4-D to both human and environment, several methods have been proposed by the researchers to remove the 2,4-D from water and soils. The summary of each of these methods such as photocatalytic degradation, advanced oxidation, electrochemical oxidation, biological treatment, ion exchange, membrane technology and activated carbon adsorption are shown in Table 2.2. Among these methods, adsorption is the most effective and widely utilized in the industry to remove hazardous organic and inorganic pollutant in water due to its simple, cost-effective process and high flexibility in the design and operation (Taktak et al., 2015; Bazrafshan et al., 2013). Adsorption is a process where the

adsorbate travels from a liquid or gas phase to form superficial monomolecular layer on a solid or liquid condensed phase (substrate) (Crawford and Quinn, 2017).

In adsorption process, it is important to ensure that a suitable adsorbent is chosen as different pollutants have different chemical structures (Bazrafshan et al., 2013). Activated carbon, carbon nanotubes and biochar are example of adsorbents for adsorption process whereby activated carbon is the most commonly used due to its attractive properties. This is because activated carbon could provide a high adsorption capacity due to its large surface area and microporous structure (Aksu and Kabasakal, 2004). According to Bahrami et al. (2018), among these three adsorbents, activated carbon give the highest removal of 2,4-D compared to carbon nanotubes and biochar from risk husk. However, biochar is found to be more economical compared to activated carbon for treatment of large volume of water. The high cost of activated carbon is mainly contributed by the raw materials and additional agents used to improve its adsorption capacity (Taktak et al., 2015).

2.4 Hydrogel application for adsorption process

Recently, hydrogel, a three dimensional polymer synthesized from one or more monomer, have gained many interests due to its relatively low cost for production and high adsorption capacity (Taktak et al., 2015). In addition, hydrogel was as an effective adsorbent, especially in the water or wastewater treatment process (Tran et al., 2018).

Generally, the hydrogel could be classified according to their shape and physicochemical properties, whereby it can be in form of hydrogel bead, hydrogel film and hydrogel nanocomposites. The hydrophilic properties of hydrogel due to its three-dimensional network and porous structure make them able to adsorb large amounts of water (Ahmed, 2015; Tran et al., 2018). Apart from its low cost and high-water retention, the hydrogel is also able to improve adsorption efficiency by entrapment of different particles inside its network (Jing et

al., 2013). Each of these particles could differ based on different types of pollutant to be adsorbed and thus, could give different advantages respectively (Tran et al., 2018). The applications of modified hydrogel according to different type of pollutant were further discussed below.

In the heavy metal ions removal, hydrogel beads based on water soluble cellulose derivative, carboxylmethyl cellulose (CMC) was successfully prepared by using inverse suspension cross-linking method with epichlorohydrin (ECH) as cross linker (Yang et al., 2010). Apart from that, hydrogel beads based on chitosan (CS) also gained interest in removal of heavy ions due to its low cost and high adsorption capacity (Jin and Bai ,2002 ; Yoshida and Takemori , 1997).

Meanwhile, hydrogel beads semi- entrapped with poly(acrylic acid-acrylamide methacrylate) and amylose into the polymer network was found to be effective adsorbent in the removal of crystal violet, a type of cationic dye (Li, 2010). However, its adsorption capacity was greatly dependent on the amylose content and pH of the solution. Thus by combining graphene oxide sheet (GO) wth polyethylenimine (PEI), a novel hydrogel beads named GO/PEI hydrogel as potential effective dye adsorbent was produced(Guo et al., 2015).

On top of that, a novel hydrogel beads by using composite matrix of CS was introduced for removal of Methyl parathion (MP), one of the pesticide used in agriculture industry (Dwivedi et al., 2014). Apart from pesticide, 2-dichlorophenoxyacetic acid (2,4-D) is one of the commonly used herbicide by the farmers for control of broad-leaved weeds in the cereal cropland, forest, pastures and even in the area adjacent to water (Aziz et al., 2018). According to study by Taktak et al. (2015), by introducing activated carbon from pomegranate husk into the polymeric network of hydrogel , the removal of 2,4-D was greatly enhanced since the adsorption capacity of the adsorbent was improved significantly.

Table 2.2: Different methods for removal of the 2,4-D from water and soils

Method of removal	Description	References
Photo catalytic degradation	The degradation of 2,4-D by different iron-mediated process with the presence of ultraviolet (UV) give higher removal of 2,4-D compared to process with UV only and without UV. Optimum degradation of 77.9% obtained in Ferrous oxalate process with usage of UV and hydrogen peroxide and pH of 2.8.	(Kwan and Chu, 2003)
Advanced oxidation	TiO_2 is used as photo-catalyst. Four system with different composition of ozone (O_3), UV and TiO_2 are observed. It is found that O_3/UV/ TiO_2 with reaction temperature of 20°C has the highest efficiency in removal of 2,4-D where higher amount of O_3 used could further enhance the process.	(Giri et al., 2007)
Electrochemical oxidation	Both electro-Fenton and photoelectron-Fenton process are studies at pH of 3.0 , where the cathode and anode used are carbon-polytetrafluoroethylene O2-fed and platinum, Pt respectively. It is found that photoelectron-Fenton process gives 83% removal of total organic content (TOC) compared to 52% removal by electro-Fenton process at 100mA of current in room conditions.	(Brillas, 2000)
Biological treatment	The biodegradation of 2,4-D is done in sequential bed reactor (SBR) operated continuously. It is found that more than 99% removal of 2,4-D is obtained in all reactors for all the hydraulic retention time (HRT) applied at “normal” feed conditions.	(Mangat and Elefsiniotis, 1999)

Table 2.2 : Continued.

Ion exchange	Ferrioxalate-exchanged resin (FOR) and ferric-exchange resin (FR) are the two catalyst used in different resin-mediated process conducted. It is found that the highest removal of 2,4-D obtained is 80% with the usage of FOR catalyst in system irradiated at 350nm of 1mM hydrogen peroxide within 60 minutes of operation.	(Kwan and Chu, 2006)
Activated carbon adsorption	Granular activated carbon (GAC) is used as adsorbent in the batch adsorption of 2,4-D. It is found that the adsorption capacity of GAC is affected by initial concentration of 2,4-D, pH and temperature. Initial pH of 2.0 and initial concentration of 2,4-D of 600 mg/L at temperature of 45°C are the optimum condition to obtain maximum adsorption capacity of GAC at 518.0 mg/g.	(Aksu and Kabasakal, 2004)
Membrane technology	Electrochemical ceramic membrane filtration was conducted without and with molecular imprinting (MI) of titanium oxide (TiO_2) into tin oxide (SnO_2) anode doped with antimony (Sb). It is found that the removal of 2,4-D using membrane with MI (62.4%) was higher than membrane technology separation without MI (29.8%) at charging voltage of 3V and flow-through mode of anode.	(Chen et al., 2020)

2.5 Statistical Analysis for Adsorption Process

2.5.1 Response Surface Methodology

Recently, many researches have use Response Surface Methodology (RSM) to generate their experiment design and analyze their results. Generally, RSM works by building empirical model that fit the best for the quantitative data. In RSM, second order model as shown in Equation 2.1 is widely used in the optimization experiment (Montgomery, 2008).

$$\hat{y} = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (2.1)$$

where $\hat{y}$ is the response or output , x_i and x_j are the input factors , β_0, β_i, β_{ii}, β_{ij} are coefficient for intercept, linear, quadratic and interaction parameters respectively and ε is residual associated to the experiments (Nair et al., 2013). For the approximation to be more accurate, higher degree of polynomial and smaller region of interest is required. However, it only suffices to proceed till second order model as transformation of the model is required if the second order is exceeded (Statease, 2021). Hence, in the RSM, the second order or the quadratic model is commonly used (Maran et al., 2013).

Witek-Krowiak et al. (2014) summarize the design of experiment using the RSM approach into six steps: 1) Screening of independent variable and responses, 2) Selection of design for experiment, 3) Execution of experiment and data collection for response, 4) Modelling of experimental data, 5) Confirmation or validation of model by means of ANOVA and obtaining the response graphs, 6) Optimization of process. Among these steps, selection of the design, for instance Central Composite Design (CCD), Full Factorial Design (FFD) and Optimal (Custom) Design are the next crucial part after screening of the variables.

The full factorial design (FFD) is able to determine the interaction between independent variable, whether the effect is low or significant to process more efficiently and flexible. A full factorial design with two level of factors is called as 2^k design, where the level of the factor

could be classify as high or low, depending on the value of the factors studied (Montgomery, 2008). The FFD may be good in the early stages of experiment, but it could lead to large sample size if more factors are involved (Natoli, 2018). The number of experiments or number of runs required for FFD can be obtained by using Equation 2.2 shown below:

$$N = p^k \tag{2.2}$$

where N is number of experiments, p is factor levels and k is number of factor (Witek-Krowiak et al., 2014). The fractional factorial design could be used instead of full factorial design if the number of runs needed to be conducted is too large. However, it could lead to some loss in information obtained compared to full factorial design (Natoli, 2018).

Apart from FFD, CCD is another alternative that could be considered as a good option when designing an experiment due to its flexibility and efficiency (Taktak et al., 2015). On top of that, CCD is good at fitting second order or quadratic polynomial (Statease, 2021). In addition, CCD could provide more information and better prediction for parameters affecting the process at lower number of runs than FFD (Witek-Krowiak et al., 2014). Basically, CCD can be divided into three types, depending on the location of axial point. Circumscribed central composite design (CCCD), inscribed central composite design (ICCD) and face centered composite design (FCCD) are the three types of CCD (Witek-Krowiak et al., 2014). Figure 2.3 shows the layout for three factors with the face centered composite design (FCCD).

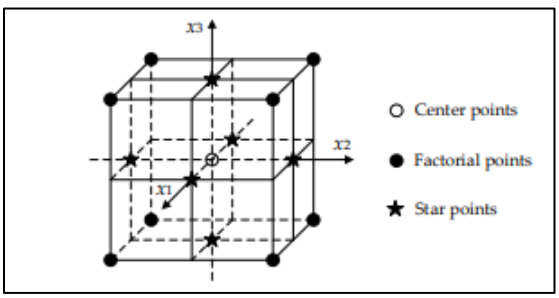

Figure 2.3: Three-factor layout for FCCD (Wang et al., 2018)

In CCD, the location and the number of centre, factorial and star points are important as they will be used to calculate the number of experiments needed with Equation 2.3 below:

$$N=2^k+2k+n_c \quad (2.3)$$

where k is number of factors, n_c is the number of center points and 2k is the star or axial point (Taktak et al., 2015).

There are some scenario or conditions where a standard response surface may not be a good or obvious choice. In this case, the Optimal Design are usually chosen. Optimal design is a flexible design, where its number of runs was determined by the selection of design criteria during the build of experiment. However, it should be noted that this design is valid and may be appropriate if and only if an irregular experimental region, nonstandard model and unusual requirement for size of sample is encountered (Anderson and Whitcomb, 2017). According to Natoli (2018), the Optimal Design are more suitable in handling experiment with more than two levels and restrictions in time as constraint compared to fractional factorial design. Thus, the selection of the design for the experiment should be made by considering all these scenarios to ensure maximum efficiency of process could be achieved.

The evaluation and confirmation of the model can be done by using analysis of variance (ANOVA) whereby it could analyze both accuracy and significance of the model developed FFD (Mourabet et al., 2014). ANOVA is based on assumption that each of value measured is a function of the three components as shown in Equation 2.4 below:

$$Y_i = \alpha_i + \beta_i + \varepsilon_i \quad (2.4)$$

where α_i is the overall value of mean, β_i is the effect of factors to output of the process and ε_i is the residual error (Witek-Krowiak et al., 2014). The arrangement and transformation of Equation 2.4 could form the equation for sum of squares for the residual errors (RSS) which is shown below:

$$RSS = \sum (Y_i - \beta_i - \alpha_i)^2 \quad (2.5)$$

In ANOVA, apart from residual error, the lack of fit, F-value and p-value are importance in the validation and quality determination of the model (Aklilu et al., 2021). The significance of the model could be indicated by the p-value whereby generally the significance level of 0.05 is chosen (Montgomery, 2008). However, if the studies conducted required extreme precision of data, lower significance level like 0.01 could be used with the probability value as indication for significance of the model (Witek-Krowiak et al., 2014).

2.5.2 Artificial Neural Network

Neural network is another mathematical alternative to the polynomials for representing data derived from statistically design of experiment. A neural network typically consists of three different layer which are the input, hidden and output layer (Kayri, 2016). The input and output layer are single layer, where the number of neurons in these layers depend on the process factor and response respectively (Awolusi et al., 2019). Meanwhile, the hidden layer can be more than one layer (Mourabet et al., 2014). According to Witek-Krowiak et al. (2014), there has yet any unique method in determining optimum number of hidden neurons as their selection is often made based on trial and error coupled with the result of empirical test. The architecture of ANN can be either simple layer or multilayer networks. Figure 2.4 shows the example of single layer architecture of neural network (Demuth et al., 1997).

Basically, the neural networks work by receiving signal from the input parameter defined by the user. The data is usually normalized within a range of 0 (new x_{min}) to 1 (new x_{max}) to obtain fast convergence and minimal root mean square error (RMSE) values. The output is then computed based on some internal calculation using the transfer function and the training of data is done to fit the target value (Sadrzadeh et al., 2008; Mourabet et al., 2014). Equation

2.6 and 2.7, 2.8, 2.9 below shows the formula that can be used for normalization of the data and the expression for different type of transfer functions respectively (Ghaedi and Vafaei, 2017):

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

$$y = logsix(x) = \frac{1}{(1 + \exp(-x))} \tag{2.7}$$

$$y = tansig(x) = \frac{2}{(1 + \exp(-2x))} - 1 \tag{2.8}$$

$$y = purelin(x) = x \tag{2.9}$$

where x_n is the normalized value of x_i, x_{min} and x_{max} are minimum and maximum value of x_i respectively . The log-sigmoid (logsig) transfer function is often used for multilayer networks whereas the sigmoid function is used for pattern recognition problem. The linear (purelin) transfer function on the other hand is suitable for function fitting problems (Ghaedi and Vafaei, 2017).

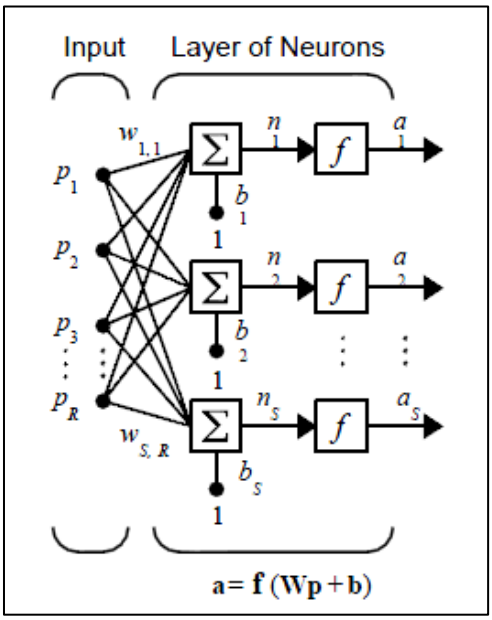

Figure 2.4: Single layer architecture of neural network (Demuth et al., 1997).

There are many trainings method for ANN such as Levenberg-Marquardt, Scaled conjugate gradient method and Bayesian method. The Levenberg–Marquardt is suitable for dealing with moderate-sized problem while Bayesian method are good in estimation for problem which have noisy and difficult inputs (Jazayeri et al., 2016). It is found that Bayesian regularization training methods have better performance in term of prediction ability compared to Levenberg–Marquardt algorithm (Kayri, 2016). However, Bayesian method require more time compared to Levenberg method due to its slower convergence (Demuth et al., 1997). Meanwhile, for Scaled conjugate gradient method, less time is needed to complete the training as its computation is faster (Doan et al., 2004) . Thus, selection of the right type of training method is important as it will affect the performance of the process.

The verification and validation of model may be performed by evaluation of the mean square error (MSE) and coefficient of determination (R^2). Higher value of R^2 and lower value of MSE indicate that the model has a good performance. Thus, the network may be trained again, or the number of hidden neurons may be changed till the optimum performance is achieved (Ghaedi and Vafaei, 2017). Equation 2.10 and 2.11 below shows the expression for MSE and R^2 respectively:

$$MSE \quad = \frac{1}{N}\sum_{i=1}^{N}\left(\left|y_{prd,i} - y_{exp,i}\right|\right)^2 \tag{2.10}$$

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left(\left|y_{prd,i} - y_{exp,i}\right|\right)^2}{\sum_{i=1}^{N}\left(\left|y_{prd,i} - y_m\right|\right)^2} \tag{2.11}$$

where N is the number of data, $y_{prd,\,i}$ is the ith predicted property characteristic, $y_{exp,i}$ is the ith measured value , y_m is the mean value of $y_{exp,i}$.

2.5.3 Application of RSM and ANN

In general, both RSM and ANN has been used widely for the purpose of modelling and optimization of many processes. Aklilu et al. (2021) compared the both ANN and RSM predictive capability for the multi-component lactoperoxidase system (LPS) by investigating the effect of temperature, storage time, concentration of sodium thiocyanate (NaSCN) and concentration of hydrogen peroxide (H_2O_2) towards the total coliform count (TCC) and total bacteria count (TBC). The optimum condition is found to be 25 ° C, 10 hours, 30 ppm of NaSCN and 18 ppm H_2O_2. The obtained result showed that the RMSE and R^2 of ANN for TCC are 3.2396 and 0.9997 while for TBC are 41.2936 and 1 respectively. Meanwhile, the RMSE and R^2 of RSM for TCC are 18.4590 and 0.9922 while for TBC are 1462.299 and 0.996 respectively. These results indicate that highly trained ANN is better than RSM model as higher R^2 and lower RMSE value indicate that the model is more accurate.

Another study is conducted by Maran et al. (2013) to predict the mass transfer parameter of osmotic dehydration of papaya by using both RSM and ANN whereby the interaction between temperature, concentration of osmotic solution and speed of agitation toward percentage of water loss, reduction of weight, and solid gain are investigated. It is found that the optimum condition of 32 °C, 60° brix of osmotic solution and 100 rpm of agitation are able to give the maximum responses. The result of ANN shows the RMSE for percentage of water loss, weight reduction and solid gain are 0.123, 0.023 and 0.003 respectively. Meanwhile, the R^2 of ANN for percentage of water loss, weight reduction and solid gain are found to be 0.992, 0.999 and 0.997 respectively. The higher R^2 and lower RMSE value of ANN compared to RSM indicate that ANN model is more accurate than RSM model. However, the summary of RSM model shows that the computational time for RSM is shorter compared to ANN.

There are also other studies for both RSM and ANN in different areas of science and engineering to compare their predictive and generalization capabilities, sensitivity analysis and

optimization abilities. Mourabet et al. (2014) conducted a study on the batch adsorption process of fluoride ion with apatitic tricalcium phosphate as adsorbent. The pH, mass of adsorbent, temperature and initial concentration of fluoride ion are varied and their effect on the adsorption capacity of fluoride are observed. The relationship between these variables and the response are demonstrated by using the quadratic polynomial model developed by Box-Behnken Design (BBD) of RSM whereby the adequacy of the model is validified by ANOVA. It is found that only temperature has positive feedback on the responses while the other variable only gives negative effect to the adsorption capacity. On top of that, the optimization of ANN model is done to compare the prediction capability of ANN with RSM. After several trials and error, it is found that 11 hidden layers are able to give the best performance. The comparison between ANN and RSM models shows that ANN is have better prediction capability than RSM. This is because the result shows that ANN has RMSE and R^2 of 0.0262 and 0.979 respectively which indicate better accuracy than RSM with RMSE and R^2 of 0.0942 and 0.927 respectively.

Apart from that, Sen et al. (2018) compared the optimization and modelling of RSM and ANN in the biosorption of chromium (VI) ions from aqueous solution using cyanobacterial biomass as bio sorbent. The interaction of initial concentration of chromium (VI), pH, temperature and amount of adsorbent towards the percentage removal of chromium (VI) are being studied in the research conducted. The second order model was employed in RSM model to prevent the aliased term in higher order model. From the RSM, the optimum condition is obtained at 81.72% removal of chromium (VI) with pH of 11, 1g/L adsorbent and 15mg/L adsorbate. Nevertheless, the ANN model is found to be able to predict the removal of chromium (VI) at various operating condition accurately than RSM. The summary for the application of both RSM and ANN model in various studies or process are shown in Table 2.3.

Table 2.3: Summary for application of RSM and ANN in various process

Application	RSM design	ANN training methods	Factors	Response	References
Activation of lactoperoxidase system for improving safety and quality of milk	Central composite design (CCD)	Levenberg–Marquardt back-propagation algorithm	Temperature, storage time, concentration of sodium thiocyanate, concentration of hydrogen peroxide	Total coliform count (TCC) and total bacteria count (TBC)	(Aklilu et al., 2021)
Mass transfer parameter prediction for osmotic dehydration of papaya	Box-Behnken Design (BBD)	Levenberg–Marquardt back-propagation algorithm	Temperature, concentration of osmotic solution and speed of agitation	Percentage of water loss, reduction of weight, and solid gain	(Maran et al., 2013)
Batch adsorption process for removal of fluoride ions	Box-Behnken Design (BBD)	Levenberg–Marquardt back-propagation algorithm	pH, mass of adsorbent, temperature and initial concentration of fluoride	Adsorption capacity of fluoride	(Mourabet et al., 2014)
Biosorption of chromium (VI) ions from aqueous solution	Central composite design (CCD)	Levenberg–Marquardt back-propagation algorithm	Initial concentration of chromium (VI), pH and amount of adsorbent	Percentage removal of chromium (VI)	(Sen et al., 2018)

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Overall Research Activity

The overall research activities are carried out as shown in Figure 3.1 below.

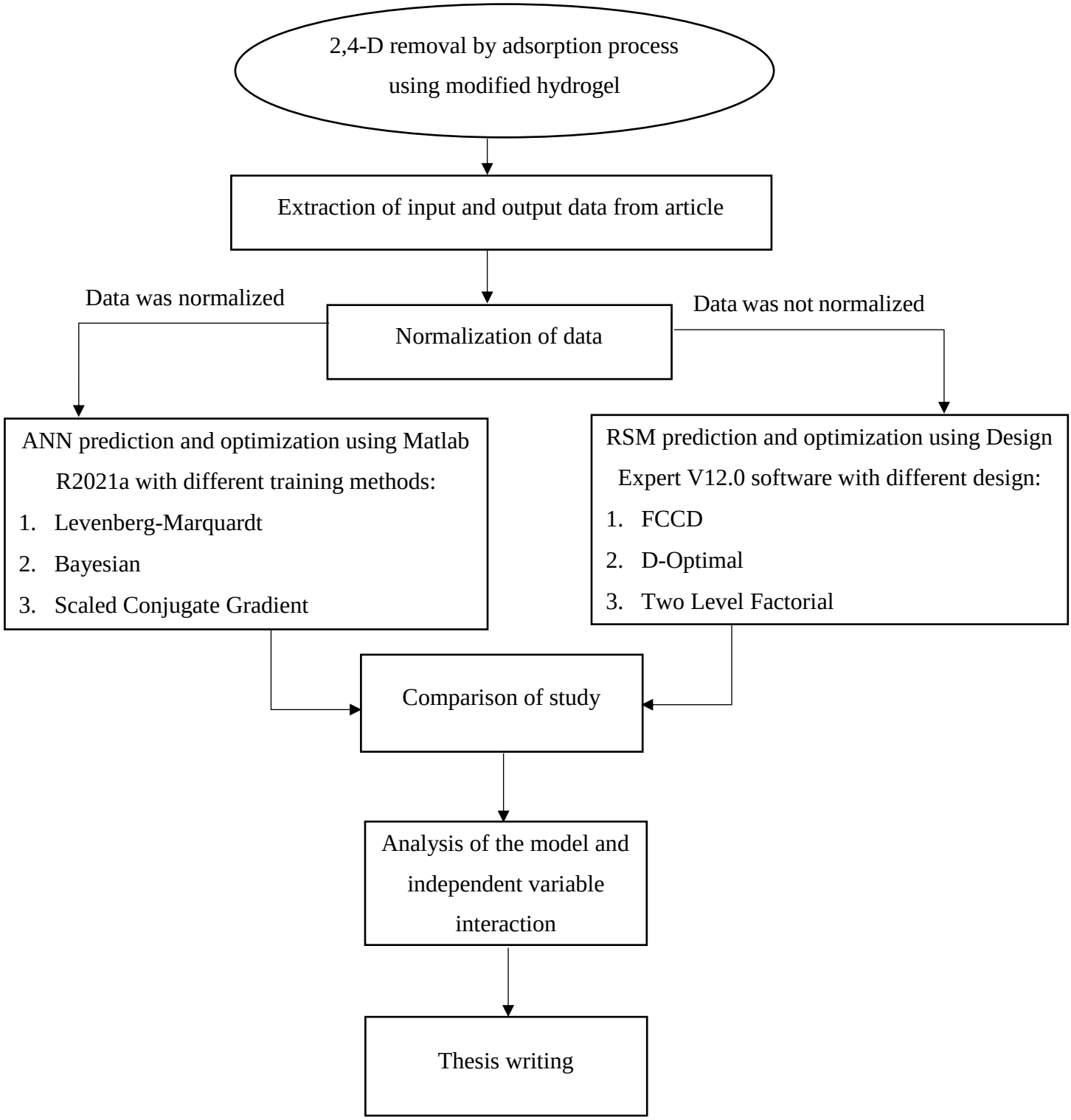

Figure 3. 1: Overall Research activities

In this study, there were no experimental work done since the experimental data was taken from previous study that has been conducted by Taktak et al. (2015). The setup and procedure for the experimental work conducted from the published study was explained in section 3.2. Meanwhile, the methodology for statistical analysis of the data in the current study were explained in Section 3.3.

3.2 Experimental Procedure

3.2.1 Preparation of Adsorbate and Adsorbents

The preparation of 2,4-Dichlorophenoxyacetic acid (2,4-D) solution as adsorbate and modified hydrogel (AC/PDMAEMA hydrogel) as adsorbent were carried out according to Taktak et al. (2015). The 2,4-D solution with purity of 98% was purchased from Sigma Aldrich. The modified hydrogel was prepared using activated carbon extracted from pomegranate husk, (Dimethylamino) ethyl methacrylate (DMAEMA) and N, N'-methylenebisacrylamide (MBAM) that were purchased from Aldrich. The in situ polymerization route described as follow was used to prepare activated carbon (AC)/poly (dimethylaminoethyl methacrylate (PDMAEMA) composite hydrogels.

About 2.5 to 20 wt % of dry activated carbon powder extracted from pomegranate husk via wave-assisted thermal treatment was inserted in 5 ml of distilled water and stirred at 500 rpm for 2 hours. The homogenous suspension solution formed was added with 20 wt% Dimethylamino (DMA) monomer and 20 mg/ml N, N′-methylenebisacrylamide (MBAM) before stirred for 1 hour. About 5 mg/ml of ammonium persulfate (APS) was then added into the solution. The polyvinylclorua (PVC) straw was used to keep the reaction mixture at room temperature for 24 hours until the gelation was completed. The gels samples obtained were then grounded into 28-mesh. Prior to this process, the AC/PDMAEMA composite hydrogel samples

were cut into small pieces, washed with bidistilled water followed by drying in vacuum oven at 50 ° C for 24 hours.

3.2.2 Adsorption process

The batch adsorption studies was conducted in the Erlenmeyer flask by changing the variables: 1) pH, 2) Initial concentration of 2,4-D , 3) Activated carbon content. In all experiment, the total volume of 2,4-D solution was kept at 10 ml. At appropriate time interval where the batch experiment ended, about 4 ml of sample of solution were taken from the Erlenmeyer flask. The initial and final concentration of 2,4-D was measured by Perkin Elmer Lambda 35 Uv-Vis spectrophotometer at 282 nm. The percentage removal of 2,4-D (%) and adsorption capacity (mg/g) could be calculated with Equation 3.1 and 3.2 respectively as shown below:

$$\text{Percentage removal of } 2{,}4-\text{D } (\%) = \frac{C_I - C_E}{C_I} \times 100 \quad (3.1)$$

$$\text{Adsorption capacity } (\text{mg/g}) = \frac{C_I - C_E}{M} \times V \quad (3.2)$$

where V is the volume of the solution (mL), M is the mass of the dry adsorbent (g) and C_I (mg/L) and C_E (mg/L) are the initial and final concentration of 2,4-D in the solutions, respectively.

3.3 Statistical Analysis

There were three factors and two responses to be analysed in the modelling and optimization for the removal of 2,4-D. The factors and response involved were shown in Table 3.1, where both RSM and ANN were used in the statistical analysis of the experimental data.

Table 3.1: List of factors and response

Factors	Response
pH	Percentage removal of 2,4-D (%)
Initial concentration of 2,4-D (mg/L)	Adsorption capacity (mg/g)
Activated carbon content (%)	

3.3.1. Response Surface Methodology (RSM)

Design Expert V12.0 was used in designing the experiment, prediction of the response, modelling and optimization of the data. The factors, as shown in Table 3.1 were varied at different range to obtain wide range of the responses. The ranges for the independent variables used in the designs of RSM in both coded and actual forms were shown in Table 3.2 whereby the factors were being varied at two levels.

Table 3.2: Range of independent variables at their coded and actual values

Factors / Independent variables	**Ranges in coded and actual values**	
	(-1)	(+1)
pH	3.00	9.00
Initial concentration of 2,4-D (mg/L)	20.00	100.00
Activated carbon content (%)	2.50	20.00

3.3.1.1 Designs of Experiment

Three design methods (FCCD, D-Optimal and 2- Level Factorial) were used in the RSM modelling and optimization. Since different designs methods have different steps in designing the experiment, the details on each of these steps were further explained in the following sections.

3.3.1.1 (a) Face Centred Composite Design

The modelling were carried out by selecting the numeric factors as shown in Table 3.2 which consist of 8 factorial point, 6 axial point and 6 centre point. Since face centred composite design was used, the value of coded distance (α) was 1. Based on value of design parameter chosen, the software generated that the number of runs needed in this design was 20, as proven with calculation in Equation 2.3.