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DESIGN OF LINEAR MODEL FOR WATER HARDNESS REMOVAL BY ACTIVATED COCONUT SHELL CARBON USING DESIGN OF EXPERIMENT METHOD

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by

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Universiti Teknologi PETRONAS,
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CERTIFICATION OF APPROVAL

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Approved by,

_____

(Dr. Lavania Baloo)

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SEPTEMBER 2017

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(DIVIYAN RAJ A/L SUNDERA RAJ)

ABSTRACT

The present study reports the water softening by adsorption of hardness ions onto Activated Coconut Shell Carbons. In the previous study, it was found that 500°C Activated Coconut Shell Carbon removed more hardness ions compared to coconut shell carbons (400, 500°C) and the other activated carbon (400°C). Therefore, 500°C ACSC was selected and used as the adsorbent for batch experiments. Characterization of Activated Coconut Shell Carbon was identified by Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy techniques. Batch experiments were carried out to determine the effect of various adsorbent factors such as adsorbent dose, pH, and contact time, on the adsorption process using synthetic water samples. Full Factorial Design with centerpoints (0,0) was used to determine the optimal values of parameters that provide the highest removal efficiency. The number of experiments carried out were based on the levels of each parameter, number of replicates and number of centerpoints. The total number of experiments was 28. The results that were run on the Design of Expert software under Full Factorial Design showed that the optimal parameter values for pH, contact time, and adsorbent dose that produced the highest percentage of calcium ion removal, which was 82.36%, were 14, 12 hours, and 0.5 g/mL respectively although significant curvature in the model was observed and the involvement of Central Composite Design for the model may be necessary. Equilibrium isotherms have been analyzed using Langmuir and Freundlich isotherm models, and the chemical reaction favored the Langmuir isotherm model meaning that the adsorption follows a monolayer approach. Kinetic study was conducted using Pseudo-First-Order and Pseudo-Second-Order equations, and it was observed that the chemical reaction suited the Pseudo-Second-Order model showing that the adsorption process was a chemical process.

Keywords: Activated Coconut Shell Carbon, Water Hardness, Adsorption, Removal Efficiency, Full Factorial Design

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Abbreviations

ACSC	Activated Coconut Shell Carbon
CAC	Commercially Activated Carbon
CSC	Coconut Shell Carbon
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
FFD	Full Factorial Design
DOE	Design of Experiment
q_e	Amount of hardness ions adsorbed per unit mass of adsorbent at equilibrium (mg/g)
c_i	Initial solute concentrations in solution (mg/L)
c_f	Final solute concentration in solution (mg/L)
m	Mass of adsorbent
C_e	Equilibrium concentration (mg/L)
K_f	Adsorption capacity factor (mg/g (L/mg)^1/n)
1/n	Adsorption intensity
a	Langmuir constant for capacity of adsorption
b	Langmuir constant for energy of adsorption
R_L	Separation factor
q_t	Amount of ions adsorbed (mg/g) at time t (hour)
K_1	Adsorption rate constant (h-1)
K_2	Adsorption rate constant (g/mg.h)
EDTA	Ethylene-diamine-tetraacetic acid
ANOVA	Analysis of Variance

CHAPTER 1
INTRODUCTION

1.1 Background

Water hardness exists due to water being in contact with divalent, soluble, metallic cations. The two main cations that cause water hardness are calcium (Ca^{2+}) and magnesium (Mg^{2+}). Other metals such as strontium, aluminum, barium, iron, manganese, and zinc also cause hardness in water, but they are not present in large concentrations in water, unlike calcium and magnesium that contribute to total hardness. Hardness is mostly expressed as milligram of calcium carbonate ($CaCO_3$) equivalent per liter and can be mentioned in terms of carbonate (temporary) and noncarbonated (permanent) hardness [1]. Water hardness due to calcium is caused by the dissolving of limestone deposits as the groundwater passes through it and for magnesium is caused by dissolving of dolomite or other magnesium bearing formations into passing groundwater. Groundwater is usually harder than surface water because of its long term contact with underground geologic formations that was mentioned previously.

Although small amounts of these minerals can be beneficial to human health in terms of nutritional value, higher dosages of these minerals in water supply can cause adverse effects not only to the individual's health but also the housing appliances that require this water supply to operate. Calcium and magnesium contributes to the formation of a "bathtub ring" which is basically precipitated soap deposited onto bathroom surfaces and also dingy laundry where the clothing becomes very irritating to the skin besides requiring more detergent than usual. Hard water forms scale, usually calcium carbonate, which is left to dry on the surface of glassware, silverware, and plumbing fixtures. Scale that forms inside water pipes eventually reduces water pipe

carrying capacity and will eventually block water flow. When hard water is heated, scale forms much faster, causing an insulation problem inside boilers, water heaters, and hot-water lines, and increases water heating costs.

Removing hardness from water is called softening and hardness is mainly caused by calcium and magnesium salts. The two basic methods of softening public water supplies are chemical precipitation and ion exchange. Other methods can also be used to soften water, such as electro-dialysis, distillation, freezing, and reverse osmosis [2]. These processes are complex and expensive and usually used only in unusual circumstances.

In Malaysia, coconut is the fourth important industrial crop after oil palm, rubber, and paddy in terms of total planted area [3]. As an industry, coconut contributes very little to the Malaysian economy therefore, using coconut wastes as a source of carbon for the purpose of hard water treatment may benefit the country financially. Coconut shell has been proven scientifically to contain high fixed carbon, low ash content and microporous structures that renders it more effective in the adsorption of gas compounds and compounds that cause color and odor variation. Activated Coconut Shell Carbon (ACSC) is a form of carbon that has a high surface area to volume relationship as well as a large network of submicroscopic pores for adsorption. The predominance of micro-pores in coconut shell carbon gives it tight structure and provides good mechanical strength and hardness and also high resistance to resist attrition or wearing away by friction. Previous studies have shown that ACSC has been used for the treatment of hard water yet its effectiveness still varies for different factors. This study is to further investigate the properties of ACSC that can be enhanced to increase the adsorption rate and hence, is the aim of this study.

1.2 Problem Statement

Treating hard water has always been a major issue in Malaysia as there are people who depend on ground water for water supply. Although this water contains minerals such as calcium and magnesium that are essential to the human body, there are many adverse effects should these minerals be consumed in a large amount. Excess of magnesium intake (above approximately 250 mg/L) in a human body may cause change in a person's daily bowel habits by giving them a laxative effect. These minerals do not only affect human health but also the wear and tear of housing appliances by forming scales in pipelines and on heating elements. Now the cost is higher as more energy is needed for the heating elements and maintenance works on the pipelines have to be done. Many methods such as chemical precipitation, ion exchange, distillation, and reverse osmosis can be used in the treatment of hard water but the cost of installation, operation and maintenance is too high. By using Activated Coconut Shell Carbon (ACSC) for treating hard water, a steady supply of activated carbon can be obtained as the material is cheap and in abundance. Even so, the effectiveness of this method is not confirmed due to varying factors.

1.3 Objectives

The objectives of this experimental study are:

- To characterize and compare the characteristics of Activated Coconut Shell Carbon (ACSC) and Coconut Shell Carbon (CSC) for water hardness removal.
- To determine the optimal Activated Coconut Shell Carbon parameter (pH, contact time, and adsorbent dose) settings to maximize the hardness removal efficiency in percentage by using the DOE based methods.
- To analyze the adsorption behavior of hardness ions onto Activated Coconut Shell Carbon (ACSC) in treating hard water by applying Freundlich and Langmuir isotherm models and conducting kinetic study.

1.4 Research Questions

The research questions for this experimental study are:

1. How does the **functional groups** present at the surface and the **average pore size** available prove the suitability of ACSC or CSC in adsorption?
2. What is the **optimal parameter** (pH, contact time, and dose) settings that will provide **highest hardness removal efficiency** in percentage and the mathematical model?
3. Does the adsorption of hardness ions follow a **monolayer** (Langmuir) or **multilayer** (Freundlich) approach and is the process a **chemical** (Pseudo-Second-Order) or **physical** (Pseudo-First-Order) process?

1.5 Scope of Study

This study focuses on maximizing the effectiveness of cation removal in synthetic and field hard water by using Activated Coconut Shell Carbon (ACSC) through varying factors and running the results in a Full Factorial Design by Design of Expert method.

For this study, the activated carbon will be produced through chemical method for the simple reason of it being more energy and cost effective when compared to physical activation. The crushed coconut shells are at first carbonized through a process called pyrolysis at a temperature of 500°C with a constant flow of nitrogen gas. The resulting charcoal is then prepared for chemical activation.

The charcoal is submerged in an aqueous strong dehydrating agent, zinc chloride for 24 hours. The charcoal is then rinsed of excess zinc chloride and soaked in distilled water for an hour before oven-dried at 100°C for 3 hours. The characteristics of the dried charcoal was then analyzed using SEM and FTIR analysis.

Batch experiments were conducted onto samples of hard water based on the design matrix with different key factors involved such as pH, contact time, and adsorbent dose. The results obtained are processed using Full Factorial Design (FFD) and the optimum values for the parameters are deduced. The optimum values are tested

in a laboratory to ensure its validity. Freundlich and Langmuir isotherm models are adopted to evaluate the adsorption process. The equilibrium data is analyzed using Kinetic models.

Finally, the results obtained are critically analyzed and documented properly as mentioned in methodology.

1.6 Significance of Study

The main aim of this research was to provide a feasible, long-term solution to this hard water problem in groundwater. This method was amongst the few methods that use recycled materials as its reactants so the cost of this treatment is considerably lower than the others. Furthermore, groundwater has proven to be a very important source of water supply be it for domestic or for industrial purposes. The increasing population on earth constitutes to the increasing demand of water supply and therefore, more water supply companies will have to diversify their modes of obtaining potable water in order to keep operating. Finally, this study is to provide knowledge in the field of research regarding hard water treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Water Hardness

Water hardness is described as the presence of multivalent metallic cations in water. Normally, these cations that are referred to have a charge greater than 1+. Minerals such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) are the most common minerals that cause hard water development. Groundwater that flow through different earth layers such as rock, gravel, soil or any underground geographic formations have these minerals deposited in them through dissolving when they are extracted later on. The geographic formations mentioned are mainly calcite ($CaCO_3$), gypsum ($CaSO_4$), and dolomite ($CaMg(CO_3)_2$).

In this research, water hardness due to calcium deposition was studied and all data collected will be in respect to concentration of calcium ions in water. This concentration of Ca^{2+} ions in water can be expressed through instrumental analysis. The total water hardness is equivalent to the sum of the molar concentrations of Ca^{2+} ions, in moles per litre (mol/L) or millimoles per litre (mmol/L) units. Water hardness is often not expressed as a molar concentration, but rather in various units, such as degrees of general hardness (dGH), German degrees (°dH), parts per million (ppm or mg/L), grains per gallon (gpg), English degrees (°e or °Clark), or French degrees (°fH). There are no standard levels as to what constitutes a hard or soft water. The tables below show the conversion factor as well as the classification for drinking water hardness.

Table 1: Classification of drinking water hardness [13]

Magnesium Hardness mg $CaCO_3$/ litre or ppm	Total Hardness mg $CaCO_3$/ litre	Clark Degrees	French Degrees	German Degrees	Hardness
<20	<50	<3.5	<5	<2.8	Soft
21-40	51-100	3.6-7.0	6-10	2.9-5.6	Moderately soft
41-60	101-150	7.1-10.5	11-15	5.7-8.4	Slightly hard
61-80	151-200	10.6-14.0	16-20	8.5-11.2	Moderately hard
81-120	201-300	14.1-21.0	21-30	11.3-16.8	Hard
>120	>300	>21.0	>30	>16.8	Very hard

2.1.1 Effects of Water Hardness

The amount of problems caused by hard water exceeds its benefits in terms of domestic and industrial usage. The measure of hardness minerals in water influences the amount of soap and detergent vital for cleaning. Soap dissolved in hard water consolidates with the minerals to produce a sticky soap curd. Showering with soap in hard water leaves a layer of sticky soap curd on the skin. The film may prevent removal of dirt and bacteria. Soap curd interferes with the return of skin to its ordinary, mildly acidic condition, and may cause irritation [19]. Soap curd on hair may make it dull, lifeless and hard to oversee.

While doing laundry in hard water, soap curds hold up in fabric amid washing to make fabric stiff and rough [20]. Deficient soil expulsion from clothing causes turning gray of white texture and the loss of brightness in colors. A sour odor can emanate from

clothes. Likewise, soap curds can deposit on dishes, bathtubs and showers, and all water apparatuses. Hard water likewise adds to wasteful and exorbitant operation of water-utilizing machines. Heated hard water forms a scale of calcium and magnesium minerals that can add to the inefficient operation or failure of water-utilizing apparatuses. Pipelines can clog up with scale that decreases water stream and at last requires pipe replacement.

2.1.2 Sources of Water Hardness

Water's hardness is controlled by the concentration of multivalent cations in the water. Multivalent cations are positively charged metal ions with a charge greater than 1+. In most cases, the cations have the charge of 2+. Ca^{2+} and Mg^{2+} are the some of the common cations found in hard water. These ions enter a groundwater supply by leaching from minerals within an aquifer. Common calcium-containing minerals are calcite ($CaCO_3$) and gypsum ($CaSO_4$). A common magnesium mineral is dolomite ($CaMg(CO_3)_2$). Although dolomite contains calcium, it mainly contributes to the leaching of magnesium into underground water streams. Rainwater and distilled water are soft, because they contain few ions [4].

2.1.3 Temporary Hardness

Temporary hardness is caused by dissolved magnesium carbonate, $MgCO_3$ and calcium carbonate, $CaCO_3$ in water. Rainwater is naturally slightly acidic because it contains dissolved carbon dioxide from the air. It reacts with the metal carbonate in rocks to form soluble calcium or magnesium ions and bicarbonate ions. Temporary hardness can be removed simply by boiling the water. When this happens, the soluble calcium or magnesium ions and bicarbonate ions react to form insoluble metal carbonate, water and carbon dioxide. This interchangeable reaction is shown in Equation 1 below [21].

$$MgCO_3\,(s) + CO_2\,(aq) + H_2O\,(l) \leftrightharpoons Mg^{2+}\,(aq) + 2HCO_3^-(aq) \qquad (1)$$

2.1.4 Permanent Hardness

Permanent hardness is mineral content that cannot be removed by boiling. When this is the case, it is usually caused by the presence of calcium sulphate, ($CaSO_4$) or calcium chloride, ($Ca(Cl)_2$) and magnesium sulphate, ($MgSO_4$) or magnesium chloride, ($Mg(Cl)_2$) in the water, which do not precipitate out as the temperature increases. Ions causing permanent hardness of water can be removed using a water softener, or ion exchange column. Equation 2 below generally shows the total permanent hardness in water samples [22].

$$\text{Total Permanent Hardness} = \text{Calcium Hardness} + \text{Magnesium Hardness} \quad (2)$$

2.2 Water Softening

Water softening is the process of removing hardness causing ions, mainly magnesium and calcium ions in water. Although having these minerals in water can have little beneficial effect to human health, the benefits of removing it from water supply is way better and can be seen in terms of lifespan of housing appliances. Some of the methods of water softening include electro-dialysis, ion-exchange, and distillation.

Electro-dialysis is a membrane separation process in which ions are transported through semipermeable membranes under the influence of an electric current or electrons from one solution to another in order to reduce the ionic content of water. People have to pre-treat water before channeling them as streams in the systems due to fouling of electro-dialysis stack [5] and maintaining this controlled environment at an optimum condition can be very tedious.

In the ion exchange process, a resin that is coated with sodium or potassium ions comes into contact with water containing calcium and magnesium ions. Two positively charged sodium or potassium ions are released for every calcium or magnesium ion that is held by the resin. This exchange happens because sodium or potassium are loosely

held by the resin. In this way, calcium and magnesium ions responsible for hardness are removed from the water, held by the resin, and replaced by sodium or potassium ions in the water [6]. Although, this process can treat both temporary hardness and permanent hardness, the cost of operating it is too high

Distillers can effectively remove most or all contaminants, including minerals, metals, organic chemicals, and microorganisms from water. The principle for operation of a distiller is simple. Water is heated to boiling in an enclosed container. As the water evaporates, the hardness causing ions, Ca^{2+} and Mg^{2+} are left behind in the boiling chamber. The steam then enters condensing coils or a chamber where the steam is cooled by air or water and condenses back to a liquid. The distilled water then goes into a storage container, usually 1.5 to 3 gallons in capacity. This method is normally used to produce pure water with little to zero contaminants. When distillation is done on a larger scale, a very high amount of energy needed. [7].

In terms of costing, the Granular Activated Carbon (GAC) water treatment system was compared to the other commercialized systems and the values obtained proved GAC treatment to be much more feasible for treating large amounts of water. The cost for treating hard water using electro-dialysis or ion-exchange process can be relatively higher as compared to the values shown in Table 2 below.

Table 2: Annual cost estimate breakdown for GAC water treatment system [32]

Item	Cost-RM/year		
	0.5 mgd	1.0 mgd	10 mgd
Capital	192927	279347	1876840
Power	10639	22144	201183
Materials	6429	7778	35079
Labor	55220	65253	201902
Total	265214	374525	2315008

2.3 Activated Carbon

Activated carbon is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption and chemical reactions [8]. Activated carbon is produced from organic, carbonaceous source materials like nutshells, wood, coconut, and coal. There are two types of activation for activated carbon, which are physical and chemical activation. Chemical activation is preferred over physical activation because the submerging of the carbon material in a chemical solution saves energy by allowing a lower activation temperature later on. Some of the main properties of activated carbon are surface area and pore size distribution. The effectiveness of these varying properties can be examined using Freundlich and Langmuir isotherm models.

2.3.1 Properties of Activated Carbon

An activated carbon product can be characterized by its activity and physical properties. Activity properties include pore size distribution that defines the available pore volume of a carbon over three pore size regions: the micropore, mesopore, and macropore regions:

- Micropore region - less than 100 Angstroms
- Mesopore region - between 100 and 1,000 Angstroms
- Macropore region - greater than 1,000 Angstroms

A broad range of pore sizes must be available, both for ease of movement of adsorbates through the carbon pores and for the adsorption of particular molecular sizes. Liquid phase carbons should contain a broader pore size distribution to remove larger organic materials, while maintaining some microporosity for the removal of taste and odor compounds. On the other hand, physical properties include surface area of the activated carbon. Surface area is basically defined as the total area provided by all possible shapes on the surface of the material. The surface areas of activated carbons are usually measured using the Brunauer-Emmett-Teller (BET) method, which employs the nitrogen adsorption at different pressures at the temperature of liquid nitrogen, which is 77K [9].

2.4 Characterization Techniques

Characterization of activated carbon is important in determining distinctive features of a carbonaceous material and distinguishing it from other materials for different uses. The characteristics of this material can be altered through its method of activation. In this analysis, two analysis were performed, which are Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR).

2.4.1 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition.

2.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum for absorption of a solid, liquid or gas. An FTIR spectrometer is able to simultaneously collect high spectral resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.

2.5 Adsorption Analysis

Water hardness can be readily determined by titration with the chelating agent, ethylene-diamine-tetra-acetic acid (EDTA). This reagent is a weak acid that can lose four H on complete neutralization. In a titration to determine the concentration of a metal ion, the added EDTA combines quantitatively with the cation to form a complex. The endpoint occurs when essentially all of the metallic cation has reacted. This EDTA titration can be used to determine the initial, C_i and final, C_f hardness in mg/L of the solution and allow the calculation of percentage removal of hardness as shown in Equation 3 below [23].

$$Percentage\ Removal = \frac{C_i - C_f}{C_i} \times 100\% \tag{3}$$

The adsorption capacity, denoted by q_e can be calculated using Equation 4 as shown below [24].

$$q_e = \frac{(C_i - C_f)V}{m} \tag{4}$$

- V represents volume of aqueous solution in litre, L
- m represents mass of adsorbent used in gram, g
- q_e represents mass of hardness ions adsorbed per mass of adsorbent at equilibrium, in mg/g

2.6 Adsorption Isotherm

The process of Adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate adsorbed on the surface of adsorbent and pressure at constant temperature. Different adsorption isotherms are Freundlich and Langmuir isotherms.

2.6.1 Freundlich Adsorption Isotherm

Freundlich isotherm is an empirical relation between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid in which it is in contact. Freundlich only applies towards physical adsorption (physisorption). Freundlich equation can be described as Equation 5 below [25].

$$q_e = KC_e^{\frac{1}{n}} \tag{5}$$

- K represents the adsorption capacity, in $(mg/g)(L/mg)^{1/n}$
- C_e is the equilibrium concentration of solute remaining in the solution, in mg/L
- 1/n represents strength of adsorption

2.6.2 Langmuir Adsorption Isotherm

Langmuir adsorption isotherm equation is generally derived using the kinetic study approach and based on some critical assumptions. These assumptions are usually not accompanied by an adequate explanation related with the mechanisms and the determination techniques of its adsorption constants [10]. These main four assumptions are:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of

adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

Langmuir isotherm for this study can be described by Equation 6 as shown below [26].

$$q_e = \frac{q_{max} K C_e}{1 + K C_e} \tag{6}$$

- q_{max} represents maximum q to form a monolayer at surface of adsorbent, in mg/g
- K represents the adsorption capacity, in $(mg/g)(L/mg)^{1/n}$
- C_e is the equilibrium concentration of solute remaining in the solution, in mg/L

The feasibility of the isotherm can be determined using the essential features of Langmuir adsorption isotherm parameter that are expressed as dimensionless constant separation factor shown in Equation 14 [30], [31].

$$R_L = \frac{1}{(1 + bC_i)} \tag{14}$$

- Ci represents initial hardness (mg/L)
- b represents Langmuir constant (L/mg)

2.7 Kinetics Study

A kinetic study of adsorption process is important to describe the controlling mechanism, which is the fundamental factor of mass transfer and cation uptake rate as well as the equilibrium time. The batch experimental data from this study will be applied to selected adsorption kinetic models, namely pseudo-first-order and pseudo-second-order models.

2.7.1 Pseudo-First-Order Model

The pseudo-first-order (Lagergren first-order) rate equation is as shown in Equation 9 below [27].

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (9)$$

- q_e is the amount of adsorbate adsorbed at equilibrium, in mg/g
- q_t is the amount of adsorbate adsorbed at time t (hour), in mg/g
- K_1 is the adsorption rate constant.

The values of K_1 and q_e can be calculated from the intercept and slope of the plots of ln ($q_e - q_t$) versus t.

2.7.2 Pseudo-Second-Order Model

The pseudo-second-order equation is also based on the sorption capacity of the solid phase and is expressed as Equation 10 below [28].

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \quad 10)$$

K_2 is the rate constant of second-order adsorption. For the same boundary conditions the integrated form becomes as shown as Equation 11 below [28].

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \left(\frac{1}{q_e}\right) t \quad 11)$$

If second-order kinetics is applicable, the plot of t/q against t of should give a linear relationship, from which q_e and K_2 can be determined from the slope and intercept of plot.

CHAPTER 3

METHODOLOGY

3.1 Concepts

3.1.1 Characterization of adsorbent

Prepared carbon and activated carbon were sent to the laboratory and two techniques were carried out to characterize both the carbons, which are Scanning Electron Microscope (SEM) technique and Fourier Transform Infrared (FTIR) technique. The SEM analysis is used to determine the external texture and crystalline structure of the material whereas the FTIR analysis is used to determine the chemical composition on the surface of the material. The SEM technique uses ZEISS Supra 55 VP Field Emission SEM while the FTIR technique uses Perkin Elmer Spectrum BX FT-IR. This analysis marks the end of phase 1.

3.1.2 Full Factorial Design (FFD) Augmented with Center Points

In many scientific investigations, the interest lies in the study of effect of two or more factors simultaneously. The factorial designs are most commonly used for this type of investigation. Several special cases of the general factorial design, namely, two-level two-factor factorial design (2^2) and three-level two-factor factorial design (3^2). These are important because they form the basis of other designs. The most important of these special cases is that of k factors, each at only two levels. Such design requires $2 \times 2 \times \cdots \times 2 = 2^k$ observations and is called "2^k Factorial Design". To distinguish it

from the class of "Fractional Factorial Design, it also called the class of "2^k Full Factorial Design" or "Full Factorial Design" (FFD) [29].

The full factorial design is the most basic experimental design which studies all possible combination of levels for k factors. The 2^k full factorial design consists of 2^k combinations of the k factors taking on two levels and a combination of factor levels is called a "run" or "treatment". These designs are widely used in factor screening experiments because there are only two levels for each factor. Therefore 2^k full factorial design provides the smallest number of runs with which k factors can be studied in a complete factorial design. The full factorial design assumes that the response variable is approximated by a first-order model (Equation 3.1) without any interaction between the factors. In Equation 3.1, y is the response variable, x_i are the factors, β_0, β_i are the coefficients, k is the number of factors and ε is the experimental error.

$$\boldsymbol{y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i} + \varepsilon \qquad (12)$$

The "2^k Full Factorial Design" cannot fit the response variable if the curvature is significant but it can detect the presence of curvature with addition of "center points" runs. Curvature is defined as the amount by which the response variable deviates from being flat [29]. Center points are created by setting all factors at their midpoint of the levels and in the coded form, center point fall at the zero level. If the curvature is significant, then the response variable represented by the first-order model (Equation 12) will not be an adequate model. In such cases, a second–order model (Equation 13) needs to be considered. In Equation 3.2, y is the response variable, x_i and x_j are the factors, β_0, β_i are the coefficients for main effects, β_{ii} is the coefficients for quadratic main effects, β_{ij} is the coefficients for two factor interaction effects, k is the number of factors and ε is the experimental error.

$$\boldsymbol{y} = \boldsymbol{\beta_0} + \sum_{i=1}^{k} \boldsymbol{\beta_i}\, \boldsymbol{x_i} + \sum_{i<j}^{k} \boldsymbol{\beta_{ij}} \boldsymbol{x_i} \boldsymbol{x_j} + \sum_{i=1}^{k} \boldsymbol{\beta_{ii}} \boldsymbol{x_i}^{\boldsymbol{2}} + \boldsymbol{\varepsilon} \tag{13}$$

3.2 Experimental Flowchart

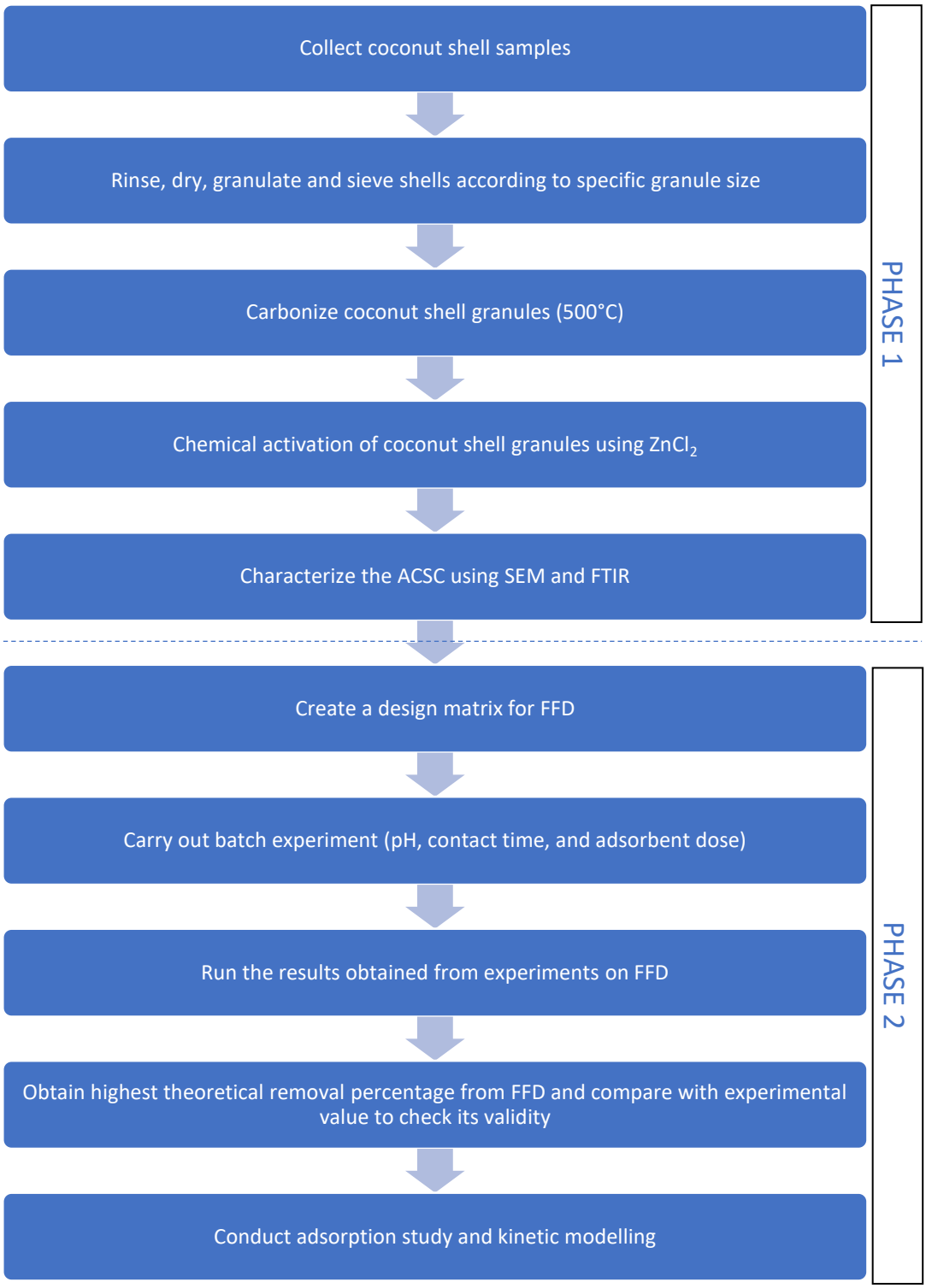

Figure 1: Flowchart for Phase 1 and Phase 2

3.3 Material

3.3.1 Stock solution

The adsorbates to be tested in this experiment is synthetic hard water, calcium nitrate ($Ca(NO_3)_2$) solution. The solution is prepared by adding aqueous calcium nitrate ($Ca(NO_3)_2.4H_2O$ to deionized water to allow calcium to float freely in its ionic form. Only one concentration of adsorbate will be prepared for this experiment using 0.511 grams of aqueous calcium nitrate diluted into 1 liter of deionized water. The resultant hardness in the water was assumed to be 250 mg/L of $CaCO_3$ (Moderately hard). This solution will represent a stock solution in this experiment.

$$\frac{0.511\ g}{236.15\ g/mol}$$

$$= 0.00216\ mol\ (Molar\ mass\ of\ Ca(NO_3)_2.4H_2O \text{ is } 236.15 \text{ g/mol})$$

$$0.00216\ mol\ \times 100\frac{g}{mol} = 0.216\frac{g}{L} = 216\frac{mg}{L}\ \left(Molar\ mass\ of\ CaCO_3\ is\ 100\frac{g}{mol}\right)$$

The above calculation shows the theoretical value of hardness in the stock solution and not the experimental value. To accurately check the amount of hardness ions in the solution, EDTA titration method was used.

3.4 Experimental Design

The batch experiments to be carried out follows the configuration of parameters shown in the design matrix below. The results obtained are to be processed in FFD.

Table 3: Factors and Levels of the Experiments

Factors	Symbols	Low level (-)	Center (0)	High level (+)
pH	A	6	10	14
Contact time (hours)	B	4	8	12
Adsorbent dose (mg/L)	C	0.1	0.3	0.5

Development of Experimental Design Layout

The number of runs needed according to 2^k full factorial experimental design for three factors ($k = 3$) was eight (2^3) and the each run was repeated twice and the author wanted to add another four centre points to provide sufficient information on possible curvature in the system. Therefore a total 28 experimental runs were required for this experiment. The experimental design layout and randomization of experiments in Table 3 was made by using *Expert-Design* software (version-10). Each row of this table represents an experiment with different combination of parameters and their levels and the respective response data is entered into this table.

Table 4: Design Matrix for batch experiments

		Factor 1	Factor 2	Factor 3	Response 1
Std	Run	A:pH	B:adsorbent dose	C:contact time	Percentage removal
			g/ml	hours	%
21	1	-1	1	1	
20	2	-1	1	1	
26	3	0	0	0	
1	4	-1	-1	-1	
10	5	1	1	-1	
13	6	-1	-1	1	
28	7	0	0	0	
2	8	-1	-1	-1	
6	9	1	-1	-1	
19	10	-1	1	1	
14	11	-1	-1	1	
24	12	1	1	1	
25	13	0	0	0	
11	14	1	1	-1	
8	15	-1	1	-1	
3	16	-1	-1	-1	
7	17	-1	1	-1	
22	18	1	1	1	
9	19	-1	1	-1	
18	20	1	-1	1	
4	21	1	-1	-1	
12	22	1	1	-1	
27	23	0	0	0	
5	24	1	-1	-1	
17	25	1	-1	1	
15	26	-1	-1	1	
23	27	1	1	1	
16	28	1	-1	1	

3.5 Experimental Setup

3.5.1 Phase 1: Preparation and Characterization of ACSC

The adsorbent used in this experiment will be coconut shell carbon and activated coconut shell carbon. The coconut shells can be obtained from the market or local grocery stores. At first, the shells are thoroughly rinsed with water to remove any form of impurities and dried under the sun for 12 hours. The sun-dried shells are crushed into smaller pieces to be fit into the granulator to obtain granulated coconut shell. The fragments are then sieved to get granules within the sizes of 0.75 to 1 mm. The granules are then stored in a container.

For the pyrolysis process, otherwise known as carbonization, the coconut shell granules were heated in a tube furnace (OTF-1200X) at a temperature of 500°C with nitrogen gas to provide an inert atmosphere. This process is to dehydrate and devolatilize the produced carbon. Around 100 g of coconut shells was placed in the furnace and carbonized at 500°C for 3 hours. The heating rate was maintained at 10°C/min with nitrogen flow of 0.5L/hour. The coconut char is now converted into activated carbon through chemical activation. This method involves submerging the granules in a strong dehydrating agent, zinc chloride ($ZnCl_2$) after pyrolysis has completed.

After the carbonization process has completed, the pieces of carbon were soaked in a 25% solution of $ZnCl_2$ for 24 hours [14]. The preparation of this solution was done by adding 25 grams of anhydrous $ZnCL_2$ into a 100 mL beaker and filling the beaker with distilled water until the 100 mL mark. The coconut shells that are to be activated are rinsed, dried with filter paper and submerged into the solution for approximately 1 hour. The granules are then filtered and placed in an oven at 100°C for 3 hours. After that, they are removed from the oven and placed in a desiccator to be cooled down to

room temperature. The activated carbon is then kept in airtight containers, ready for batch experiments.

3.5.2 Phase 2: Batch Experiments and Optimization on FFD

There were several factors experimented to study the adsorption behavior of ACSC on the removal of water hardness. Those parameters were pH (6, 8, 10, 12, 14), contact time (4, 6, 8, 10, 12 hours), and adsorbent dose (0.100, 0.200, 0.300, 0.400, 0.500 g/mL). Since FFD is used, only the highest, lowest and middle values of parameters are to be tested at all possible combinations first. The number of combinations is dependent upon number of levels and variables and in this case since the levels and variables are 2 and 3 repectively, there are 8 possible combinations. To obtain a more accurate result, replication was done twice resulting in 24 experiments. There are 4 centerpoints added to reduce error in readings, totaling up to 28 experiments. The data obtained from the experiment is then tabulated with the numbers -1, 0, and 1 denoting the lowest, middle, and highest value for the parameter. This result becomes the database for FFD system.

As for the batch experiments, since the first configuration shows (-1,-1,-1), all the parameters are tested at their minimum levels. A 250 mL conical flask was prepared and 100 mL of synthetic hard water (216 mg/L as CaCO3) was measured and poured into it. The pH value of the solution was adjusted to the value of 4 using either sodium hydroxide (NaOH) or dilute hydrochloric acid (HCl). A dose of 0.025 g/ml of activated carbon was added into the solution. The conical flask was then placed in an orbital shaker at 150 rotations per minute for a contact time of 2 hours. The solution was then filtered using Grade 1 Whatman filters and the filtrates were analysed by measuring the final water hardness through EDTA titration. These same steps were followed for the remaining 27 experiments with the configurations as shown in the table. The results obtained are tabulated in the design matrix.

The Design-Expert (Version-10) software was used to analyse the response data of the water hardness removal efficiency in percentage from Table 3. These data were entered into the software data sheet and the software statistical function was used to analyse the experimental result. The following steps are involved in the analysis:

i. Perform a transformation if desired.
ii. Identify the significant effect of factors by half-normal plot.
iii. Analysis of variance (ANOVA).
iv. Modelling of the responses.
v. Validation of the modelling responses equations.
vi. Model adequacy check by residual analysis.
vii. Determine the optimal process parameters setting by response surface and contour plots.

3.6 Key Milestones

3.6.1 Key Milestone for FYP 1

Week 2	• Confirmation of FYP title
Week 4	• Defined Problem Statement, Objectives, and Scope of study
Week 6	• Submission of Extended Proposal
Week 8	• Preliminary lab work
Week 9	• Prepared for Proposal Defence
Week 12	• Completed Research and Literature review
Week 14	• Submission of Interim Report

3.6.2 Key Milestone for FYP 2

Week 2	• Preparation of Activated Coconut Shell Carbon (ACSC)
Week 5	• Submission of ACSC samples for surface characterization
Week 7	• Completed Testing All Parameters for Batch Experiments
Week 8	• Carrying out Full Factorial Design (FFD) for Batch Experiments
Week 9	• Compilation of Data and Analysis
Week 12	• Submission of Draft Final Report
Week 13	• Submission of Dissertation and Technical Paper
Week 15	• Viva

3.7 Gantt Chart

3.7.1 Gantt Chart for FYP 1

No	Activities	Planning Period (Week)													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of FYP title														
2	Preliminary Research Work														
3	Determining Problem Statement and Objectives														
4	Identifying Work Scope														
5	Research and Literature Review														
6	Submission of Extended Proposal														
7	Preliminary Lab Work														
8	Preparation for Proposal Defence														
9	Proposal Defence														
10	Preparation of Interim Report														
11	Submission of Interim Report														

3.7.2 Gantt Chart for FYP 2

No	Activities	Planning Period (Week)													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Preparation of CAC and ACSC														
2	SEM and FTIR characterization														
3	Submission of Progress Report														
4	Carrying out Batch Experiment														
5	Freundlich and Langmuir Adsorption Isotherm Analysis														
6	FFD Analysis based on DOE														
7	Batch Experiment for selected cases														
8	Compile Data and Analysis														
9	Pre-SEDEX														
10	Submission of Draft Final Report														
11	Submission of Dissertation (Softbound)														
12	Submission of Technical Paper														
13	Viva														
14	Submission of Project Dissertation (Hardbound)														

CHAPTER 4

RESULTS AND DISCUSSION

The optimal ACSC used in the batch experiments were prepared using parameter settings obtained from a previous study conducted in Universiti Teknologi Petronas. In this study, three temperatures were chosen to carry out carbonization of coconut shell granules. These temperatures were 300°C, 400°C, and 500°C. It was noticed that at 300°C, the granules did not carbonize completely and the temperature was immediately rejected. The two remaining temperatures considered were then split into two categories, namely Coconut Shell Carbon (CSC) and Activated Coconut Shell Carbon (ACSC). The ACSC differs from the CSC as it had been activated chemically under controlled conditions. These two carbons were tested in terms of adsorption capacity and the ACSC produced from 500°C showed most percentage of adsorption. SEM and FTIR analysis were used to describe the characteristics of ACSC that made it better than CSC. It was found that the ACSC had a higher total surface area due to a large network of microscopic pores found within the granules.

4.1 Preparation of ACSC

4.1.1 Moisture Content

$$\boldsymbol{MC = \frac{Initial\ weight - Oven - dry\ weight}{Oven - dry\ weight} \times 100} \tag{14}$$

1. **Batch 1**

   Weight of coconut shell before pyrolysis = 137.715 grams

   Weight of coconut shell after pyrolysis = 44.49 grams

$$MC = \frac{137.715 - 44.49}{44.49} \times 100 = 209.54\%$$

2. **Batch 2**

   Weight of coconut shell before pyrolysis = 137.322 grams

   Weight of coconut shell after pyrolysis = 44.983 grams

$$MC = \frac{137.322 - 44.983}{44.983} \times 100 = 205.27\%$$

An average of 207.41% of moisture content is estimated per batch of carbonized coconut shells. Moisture content is a very important factor when relating to adsorption capacity. Adsorption relies on total surface area available for reaction and also porosity of given material. High moisture content may cause all porous sites to be filled with water and prevent adsorption of the chemicals to be tested. Also, a high moisture content of adsorbent shows that the porosity of adsorbent is high and more sites are available for adsorption.

4.1.2 Pyrolysis

The sample was placed in a tube furnace for 3 hours starting 8.00 a.m. in the morning but only collected at 4.00 p.m. in the evening as the sample and the furnace requires a considerable amount of time for cooling down.

Figure 2: 500°C Activated Coconut Shell Carbon

4.2 Characterization of Adsorbent

4.2.1 Scanning Electron Microscope (SEM) Analysis

4.2.1.1 Coconut Shell Carbon (CSC)

The images obtained are the SEM images of coconut shell carbon that has undergone pyrolysis at 500°C. Notice that the surface does not have much pores for adsorption. This means that this form of carbon produced is unsuitable for water treatment by adsorption. The average pore diameter recorded for CSC is 1.237 µm.

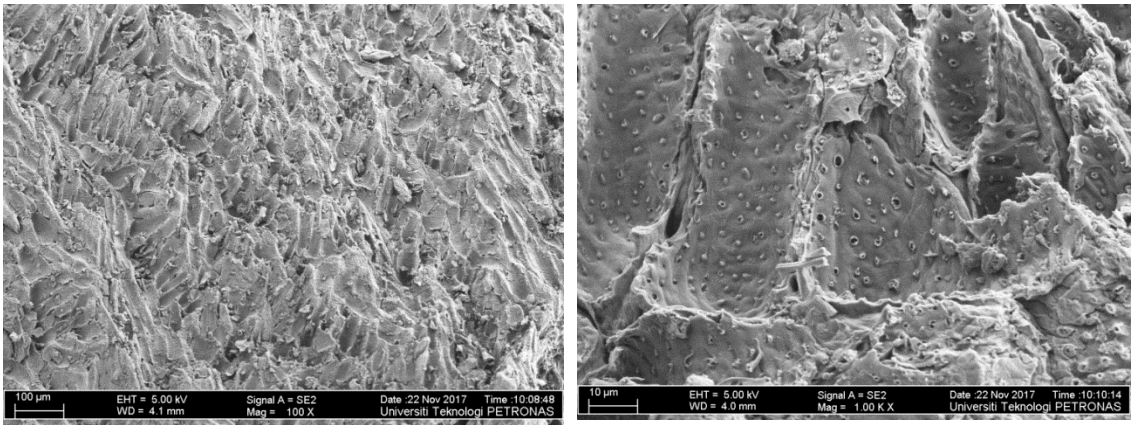

Figure 3: 500°C CSC SEM image (100 x, 1.00 k x)

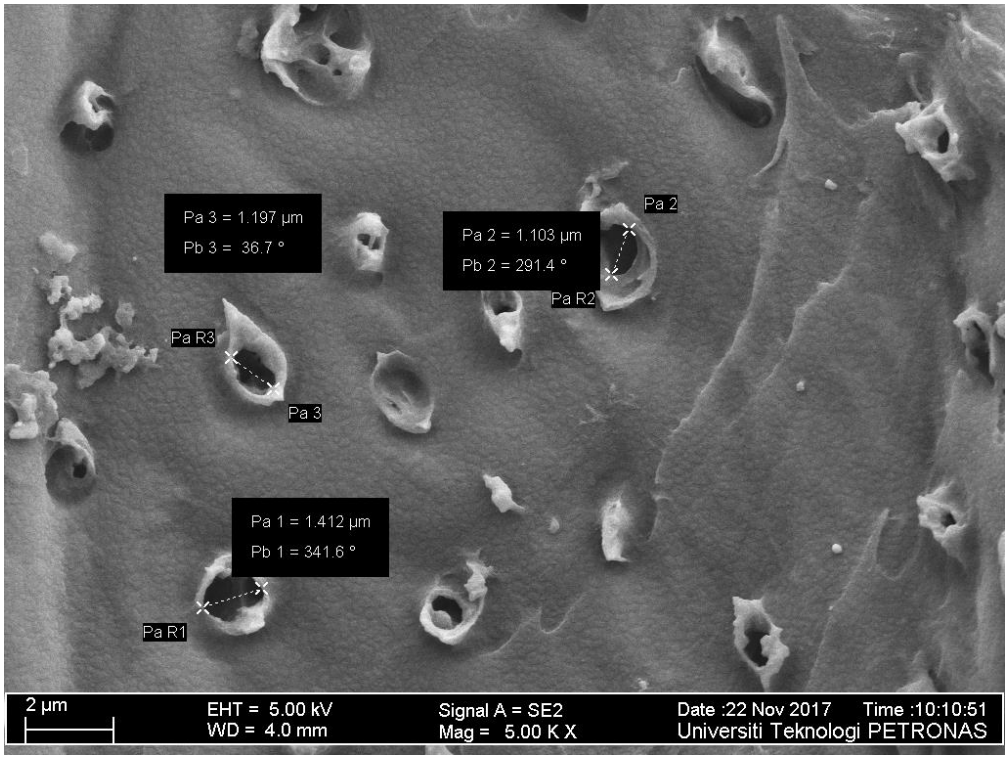

Figure 4: 500°C CSC SEM image with pore size (5.00 k x)

4.2.1.2 Activated Coconut Shell Carbon (ACSC)

The images shown below is the SEM images for activated coconut shell carbon that has been carbonized at 500°C. From the images provided, it is visible that the surface is more porous than that of CSC and also its pores are larger in diameter. The average pore diameter of ACSC is 7.377 µm.

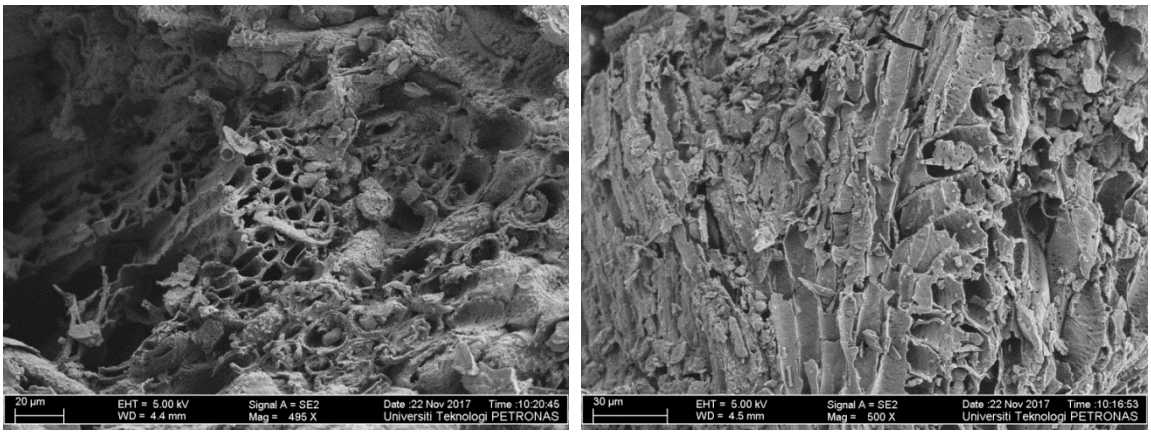

Figure 5: 500°C ACSC SEM images (500 x, 495 x)

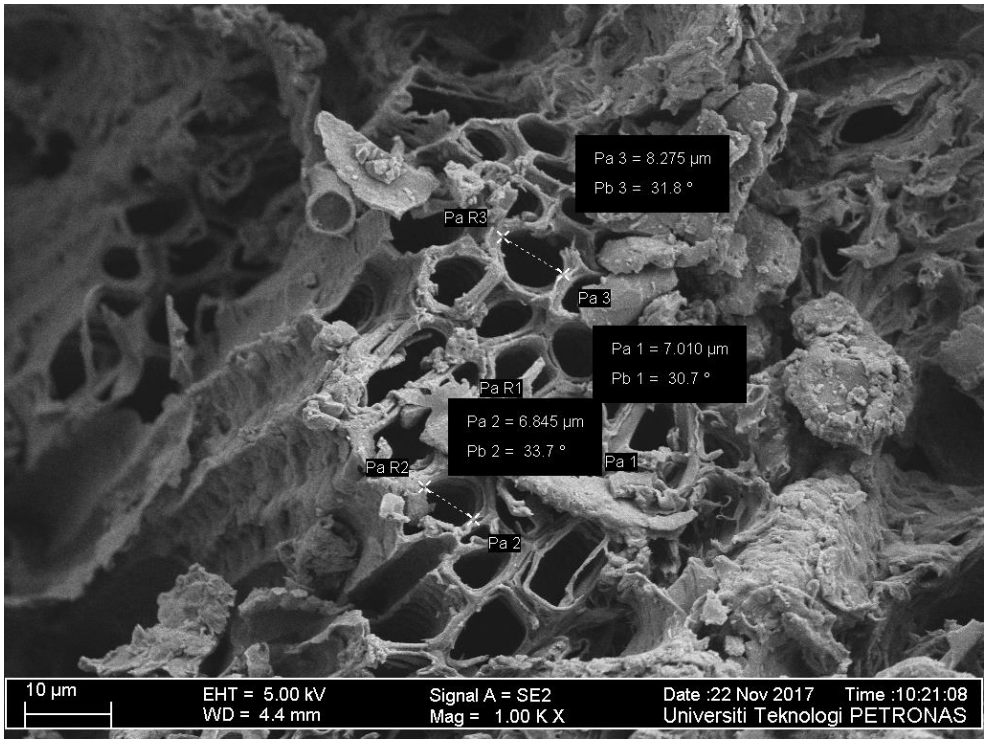

Figure 6: 500°C ACSC SEM images and pore diameter (1.00 k x)

4.2.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

4.2.2.1 Coconut Shell Carbon (CSC)

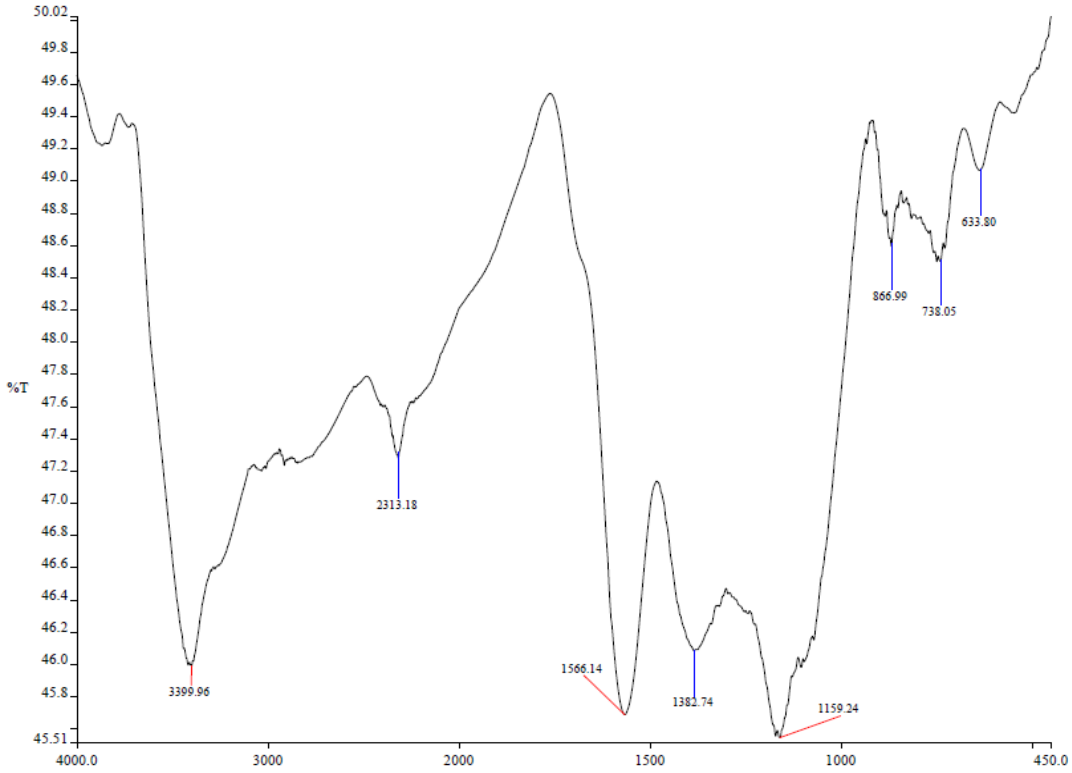

Figure 7: FTIR spectrum for 500°C CSC

In Figure 7, the peaks at 3399.96, 2313.18, 1566.14, 1382.74, 1159.24, 866.99, 738.05, and 633.80 cm^{-1} represents strong alcohol O-H stretching, strong carbon dioxide O=C=O stretching, strong nitro compound N-O stretching, medium alkane C-H bending, strong tertiary alcohol C-O stretching, strong halo compound C-Cl stretching, strong alkene C=C bending, and strong halo compound C-Br stretching respectively.

4.2.2.2 Activated Coconut Shell Carbon (ACSC)

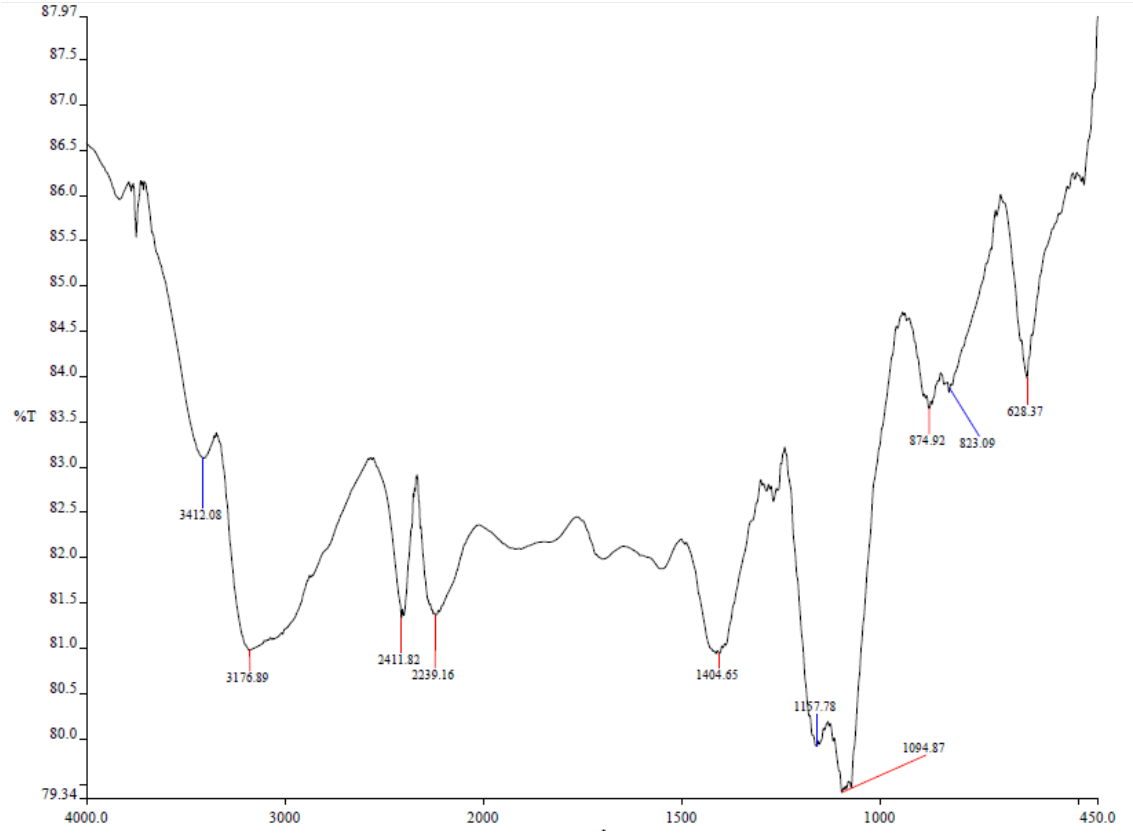

Figure 8: FTIR spectrum for 500°C ACSC

In Figure 8, the peaks at 3412.08, 3176.89, 2411.82, 2239.16, 1404.65, 1157.78, 1094.87, 874.92, and 823.09 signify strong alcohol O-H stretching, weak alcohol O-H stretching, weak thiol S-H stretching, weak alkyne CΞC stretching, medium alkane C-H bending, strong tertiary alcohol C-O stretching, strong secondary alcohol C-O stretching, strong 1, 2, 4-trisubstituted C-H bending, and strong 1, 2, 4-trisubstituted C-H bending respectively.

4.3 Full Factorial Design

4.3.1 Half-Normal Plot

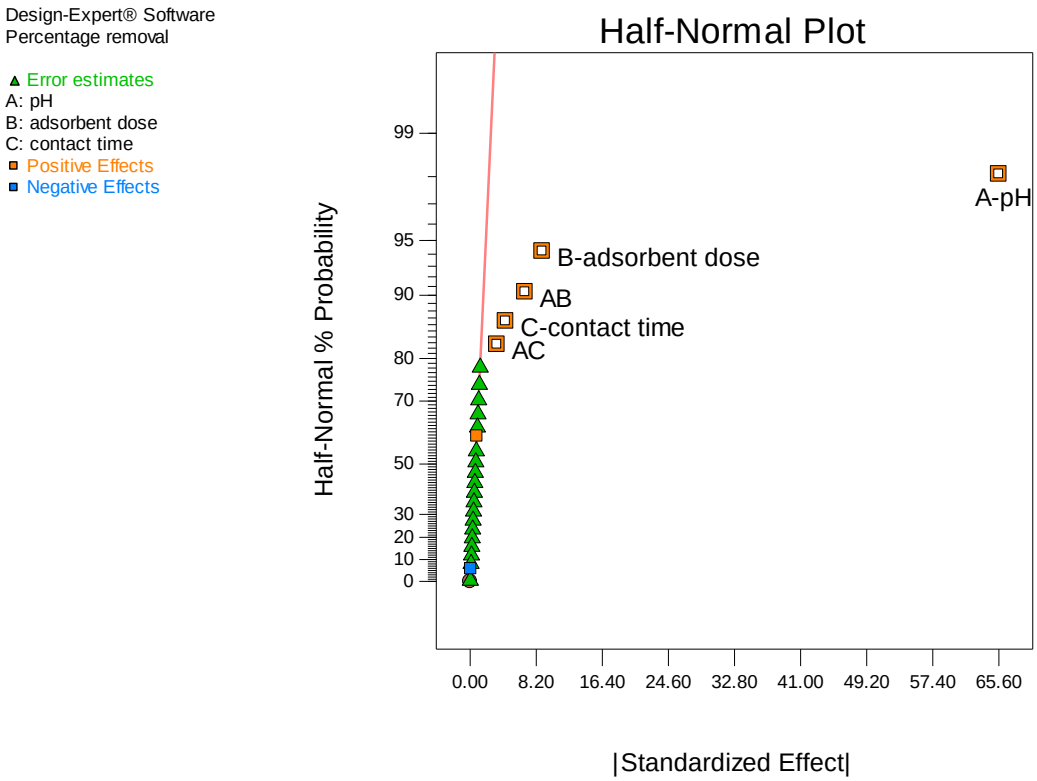

Figure 9: Half-Normal Plot for relationship between three parameters

The half-normal plot describes the factors or combination of factors that affect the response the most. By default the red "error line" will be placed such that it represents the smallest 50% of the effects. It is intended to be a visual guide to assist with selecting effects. The unimportant effects should line up on a line near zero. The factor with the highest gap shows the most effect on the response, which is in this case the pH of the solution.

All the effects that are off the line were selected starting from the right to the left. In this case, the last effect is factor AC. There is a big gap between AC and the smaller effects that line up near zero. This gap is often a good indication to stop selecting effects.

4.3.2 Analysis of Variance (ANOVA)

Response 1: Percentage removal

If there are center points detected, The ANOVA is presented in two ways:

a) **Adjusted model**: The factorial model includes a curvature term, which separates the curvature from the lack-of-fit sum of squares. The adjusted model provides the factorial model coefficients the author would get if there were no center points and is used for diagnostics (by default).
b) **Unadjusted model**: The model coefficients are fit using all the data (including the center points) without a curvature term. The unadjusted model is used to create the model graphs and for optimization predictions.

ANOVA Summary

Table 5: Summary of ANOVA

	Adjusted	**Model**		**Unadjusted**	**Model**	
	F-value	**p-value**		**F-value**	**p-value**	
Model	944.86	< 0.0001	significant	147.33	< 0.0001	significant
Curvature	120.09	< 0.0001	significant			
Lack of Fit	0.37	0.6989		37.85	< 0.0001	significant

Curvature appears significant. By default, Design-Expert considers values of ≤ 0.05 to be significant. Significant curvature depicts that the endpoint is still not reached and that the experiment is moving towards Central Composite Design (CCD).

Model Summary

Table 6: Model Summary

	Adjusted	Model	Unadjusted	Model
	Coefficient		Coefficient	
Factor	**Estimate**	**p-value**	**Estimate**	**p-value**
Intercept	33.93		31.92	
A-pH	32.80	< 0.0001	32.80	< 0.0001
B-adsorbent dose	4.48	< 0.0001	4.48	0.0015
C-contact time	2.20	0.0002	2.20	0.0872
AB	3.41	< 0.0001	3.41	0.0111
AC	1.67	0.0025	1.67	0.1890
Ctr Pt 1	-14.09	< 0.0001		

Unadjusted R-squared values give the percentage of explained variation as if all independent variables in the model affect the dependent variable, whereas the adjusted R-squared gives the percentage of variation explained by only those independent variables that in reality affect the dependent variable. R-squared cannot verify whether the coefficient ballpark figure and its predictions are prejudiced. It also does not show if a regression model is satisfactory, it can show an R-squared figure for a good model, or a high R-squared figure for a model that doesn't fit. The p-value is the area to the right of the F statistic, obtained from ANOVA table. It is the probability of observing a result (F-critical) as big as the one which is obtained in the experiment, assuming the null hypothesis is true. Low p-values are indications of strong evidence against the null hypothesis.

Table 7: ANOVA for selected factorial model (diagnostic plots)

ANOVA for selected factorial model						
Analysis of variance table [Partial sum of squares - Type III]						
	Sum of		**Mean**	**F**	**p-value**	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	26765.25	5	5353.05	944.86	< 0.0001	significant
A-pH	*25822.13*	*1*	*25822.13*	*4557.83*	*< 0.0001*	
B-adsorbent dose	*480.88*	*1*	*480.88*	*84.88*	*< 0.0001*	
C-contact time	*116.47*	*1*	*116.47*	*20.56*	*0.0002*	
AB	*279.01*	*1*	*279.01*	*49.25*	*< 0.0001*	
AC	*66.77*	*1*	*66.77*	*11.78*	*0.0025*	
Curvature	680.39	1	680.39	120.09	< 0.0001	
Residual	118.97	21	5.67			
Lack of Fit	*4.40*	*2*	*2.20*	*0.37*	*0.6989*	*not significant*
Pure Error	*114.57*	*19*	*6.03*			
Cor Total	27564.61	27				

The ANOVA above is for a model that adjusts for curvature. This is the default model used for the diagnostic plots.

Table 8: ANOVA for selected factorial model (prediction plots)

ANOVA for selected factorial model						
Analysis of variance table [Partial sum of squares - Type III]						
	Sum of		**Mean**	**F**	**p-value**	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	26765.25	5	5353.05	147.33	< 0.0001	significant
A-pH	*25822.13*	*1*	*25822.13*	*710.68*	*< 0.0001*	
B-adsorbent dose	*480.88*	*1*	*480.88*	*13.23*	*0.0015*	
C-contact time	*116.47*	*1*	*116.47*	*3.21*	*0.0872*	
AB	*279.01*	*1*	*279.01*	*7.68*	*0.0111*	
AC	*66.77*	*1*	*66.77*	*1.84*	*0.1890*	
Residual	799.36	22	36.33			
Lack of Fit	*684.79*	*3*	*228.26*	*37.85*	*< 0.0001*	*significant*
Pure Error	*114.57*	*19*	*6.03*			
Cor Total	27564.61	27				

The ANOVA above is for a model that does not adjust for curvature. This is the default model used for prediction and model plots.

The Model F-value of 147.33 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, AB are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The "Lack of Fit F-value" of 37.85 implies the Lack of Fit is significant. There is only a 0.01% chance that a "Lack of Fit F-value" this large could occur due to noise. Significant lack of fit is bad, the model should be fit.

Std. Dev.	6.03	R-Squared	0.9710
Mean	31.92	Adj R-Squared	0.9644
C.V. %	18.88	Pred R-Squared	0.9647
PRESS	973.52	Adeq Precision	28.298
-2 Log Likelihood	173.31	BIC	193.30
		AICc	189.31

Figure 10: Standard deviation, Mean & R-squared values

The "Pred R-Squared" of 0.9647 is in reasonable agreement with the "Adj R-Squared" of 0.9644. For example, the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 28.298 indicates an adequate signal. This model can be used to navigate the design space.

Table 9: Effectiveness of parameters on results

	Coefficient		**Standard**	**95% CI**	**95% CI**	
Factor	**Estimate**	**df**	**Error**	**Low**	**High**	**VIF**
Intercept	31.92	1	1.14	29.56	34.28	
A-pH	32.80	1	1.23	30.25	35.35	1.00
B-adsorbent dose	4.48	1	1.23	1.92	7.03	1.00
C-contact time	2.20	1	1.23	-0.35	4.75	1.00
AB	3.41	1	1.23	0.86	5.96	1.00
AC	1.67	1	1.23	-0.88	4.22	1.00

The table above shows the influence of the tested factors on the experiment. The pH value has the highest effect on the percentage removal of calcium ion indicating that this is one of the main parameters that need to be considered the next time a similar design run is conducted. The 95% confidence interval defines a range of values that can

be 95% certain contains the population mean. Therefore in this case the most mean values of the experimental results can be found under pH factor.

4.3.3 Modelling of the response

4.3.3.1 Interaction Plot

4.3.3.1.1 Adsorbent dose-pH Interaction Plot

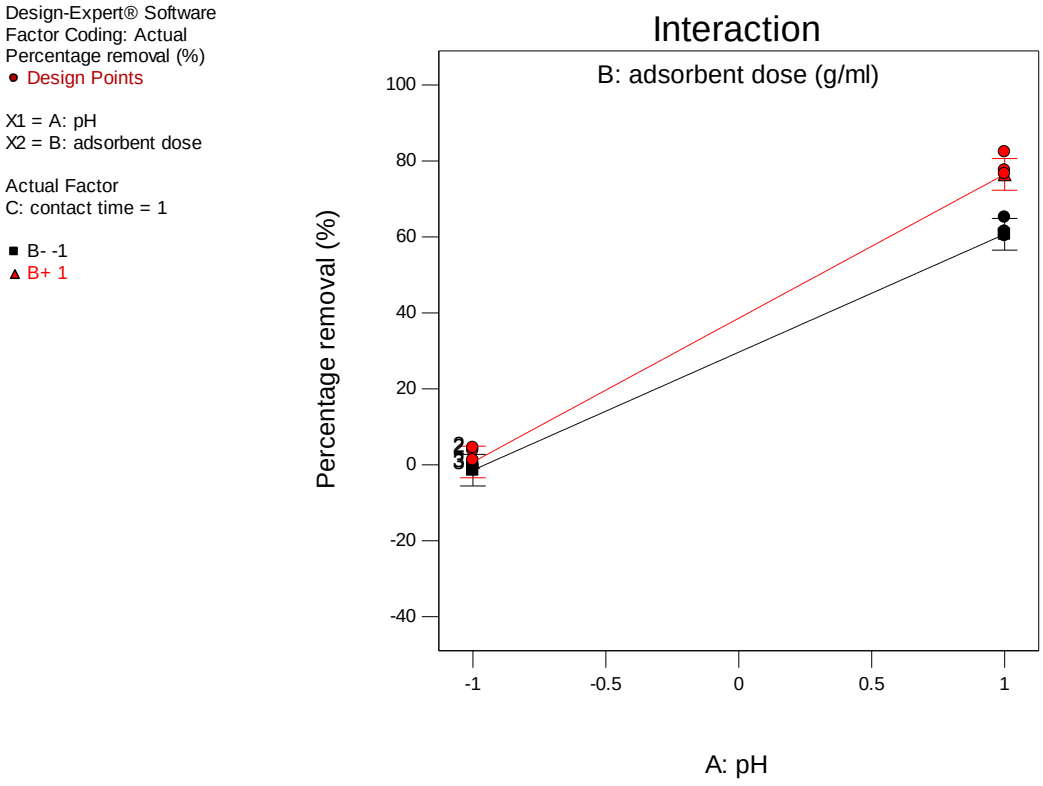

Figure 11: Adsorbent dose-pH Interaction Plot

The "I-Beam" symbols on this plot depict the 95% Least Significant Difference (LSD) interval for the plotted points. Those points that have non-overlapping intervals (for example, the LSD bars don't intersect or overlap from left to right through an imaginary horizontal line) are significantly different.

The spread of the points on the right side of the graph (where pH is high) is bigger than the spread between the points at the left side of the graph (where pH is low.)

In other words, the effect of adsorbent dose (B) is less significant at the low level of pH (A). Therefore, the experiments must go to high pH and high adsorbent dose in order to increase the percentage of removal. This combination is represented by the red triangle symbol at the upper right of the interaction plot.

4.3.3.1.2 Contact time-pH Interaction Plot

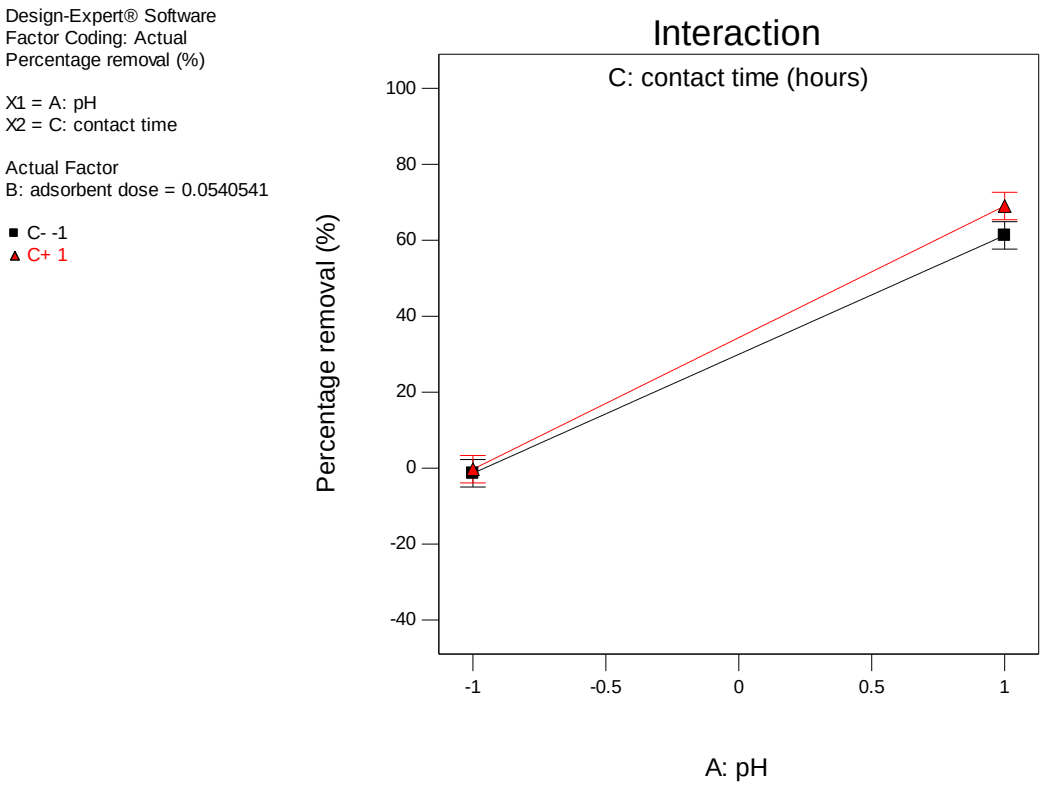

Figure 12: Contact time-pH Interaction Plot

The spread of the points on the right side of the graph (where pH is high) is bigger than the spread between the points at the left side of the graph (where pH is low.) In other words, the effect of contact time (C) is less significant at the low level of pH (A). Therefore, the experiments must go to high pH and high contact time in order to

increase the percentage of removal. This combination is represented by the red triangle symbol at the upper right of the interaction plot.

4.3.3.2 Cube Plot

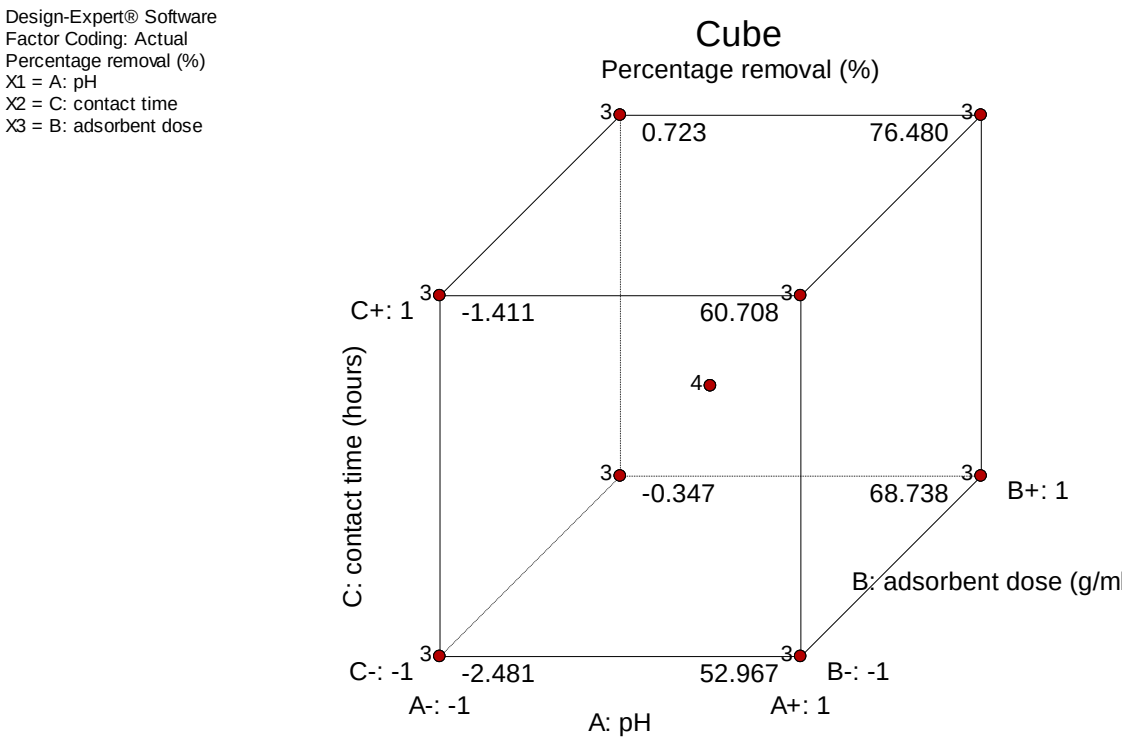

Figure 13: Cube Plot

This plot shows how three factors combine to affect the response. All values shown are predicted values, thus allowing plots to be made even with missing actual data. Because the factors of interest here are A, B, and C, the program picked them by default. Percentage removal is maximum at settings A+, B+, C+ (upper rear right corner with predicted response over 76).

4.3.3.3 3D-Surface Plot

4.3.3.3.1 Contact time-pH Surface Plot

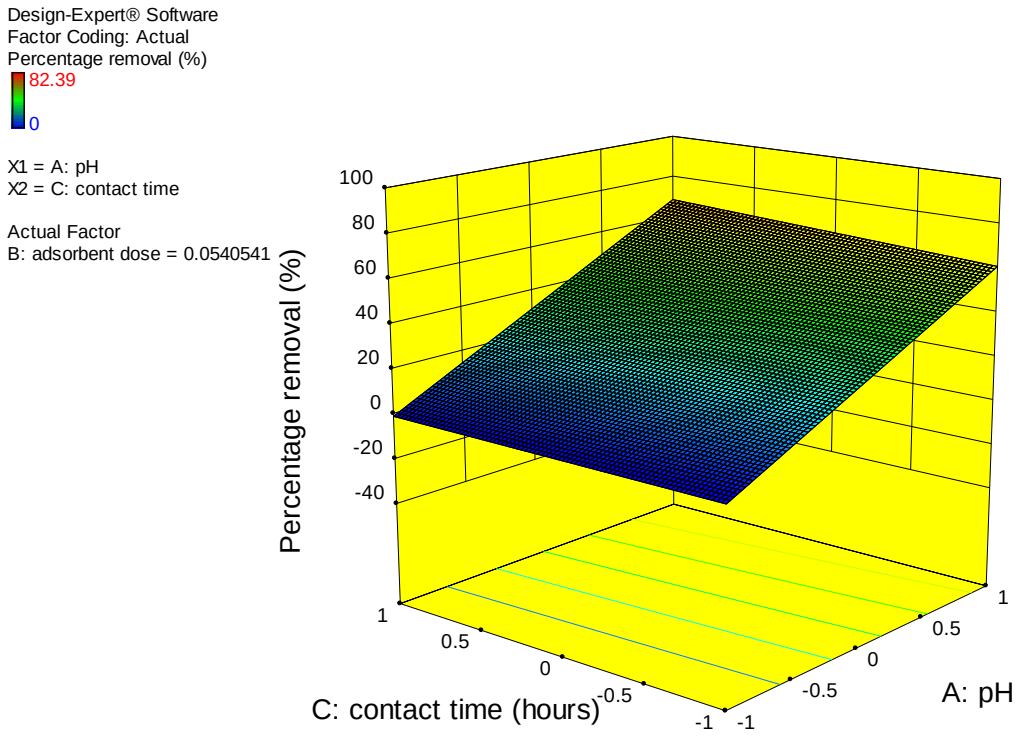

Figure 14: Contact time-pH Surface Plot

This surface plot simply depicts the percentage removal by interaction between contact time and pH at a fixed adsorbent dose value. The representation of the results takes a planar form proving that the results obtained were in a uniform manner. The values of pH and contact time are in a coded system.

4.3.3.3.2 Adsorbent dose-pH Surface Plot

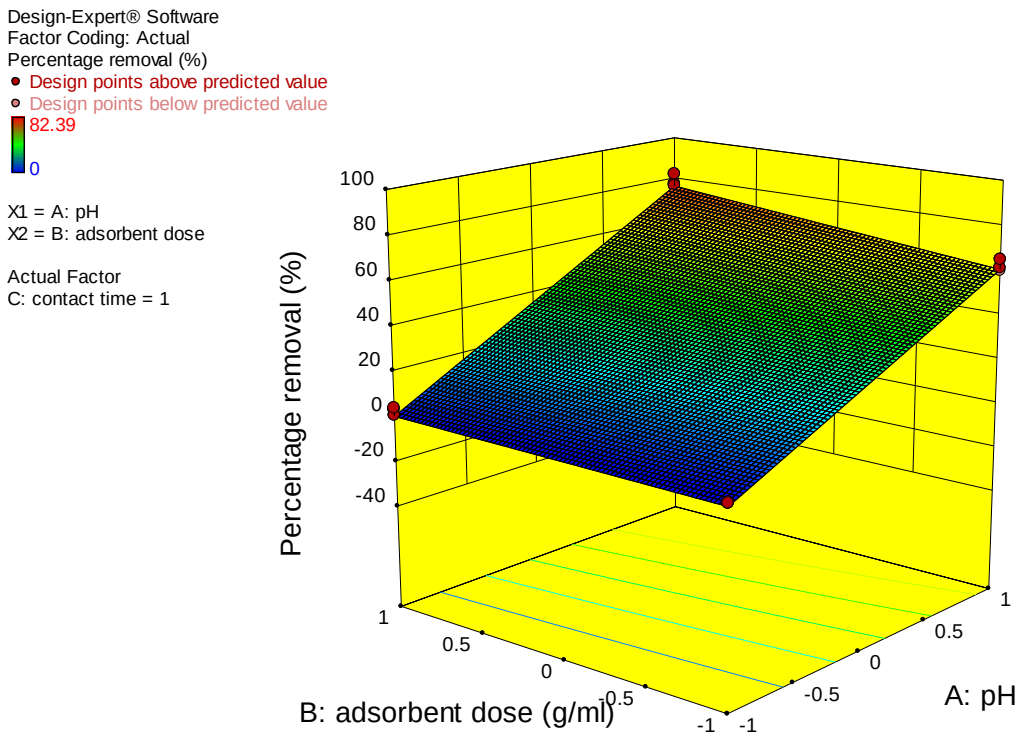

Figure 15: Adsorbent dose-pH Surface Plot

This surface plot simply depicts the percentage removal by interaction between adsorbent dose and pH at a fixed contact time value. The representation of the results takes a planar form proving that the results obtained were in a uniform manner. The values of pH and adsorbent dose are in a coded system.

4.3.4 Regression Equation

Final Equation in Terms of Coded Factors:

Percentage removal =
+31.92
+32.80 * A
+4.48 * B
+2.20 * C
+3.41 * AB
+1.67 * AC

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels of the factors are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Final Equation in Terms of Actual Factors:

Percentage removal =
+31.92214
+32.80125 * pH
+4.47625 * adsorbent dose
+2.20292 * contact time
+3.40958 * pH * adsorbent dose
+1.66792 * pH * contact time

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

4.3.5 Model Adequacy check by Residual Analysis

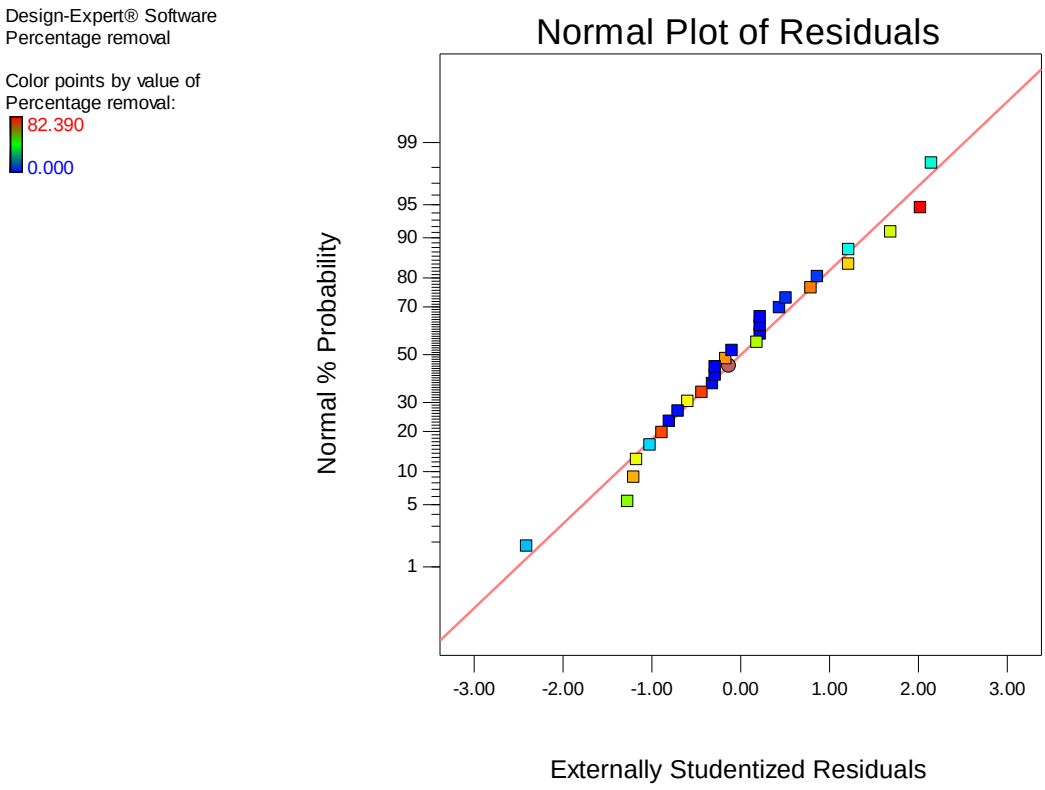

Figure 16: Residual Analysis

By default, residuals are studentized, meaning it is essentially a conversion to standard deviation scale. Also, they are done externally, that is, with each result taken out before calculating its residual. Statisticians refer to this approach as a "case-deletion diagnostic." If something goes wrong in the experiment or measurement and it generates a true outlier for a given run, the discrepant value will be removed before assessing it for influencing the model fit. This improves the detection of any abnormalities.

Ideally the normal plot of residuals is a straight line, indicating no abnormalities. The data doesn't have to match up perfectly with the line. A good rule of thumb is called the "fat pencil" test. If you can put a fat pencil over the line and cover up all the data points, the data is sufficiently normal. In this case the plot looks acceptable so other analysis can be done.

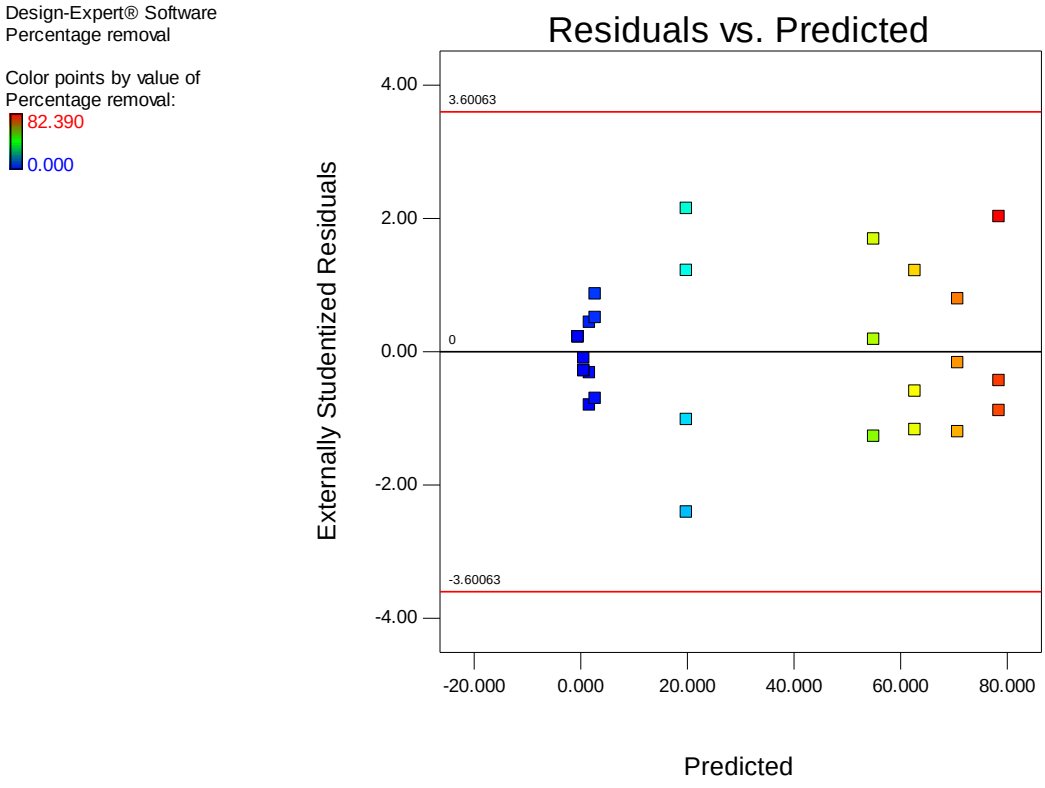

Figure 17: Residuals versus Predicted Analysis

The size of the residual should be independent of its predicted value. In other words, the vertical spread of the studentized residuals should be approximately the same across all levels of the predicted values. In this case the plot looks acceptable.

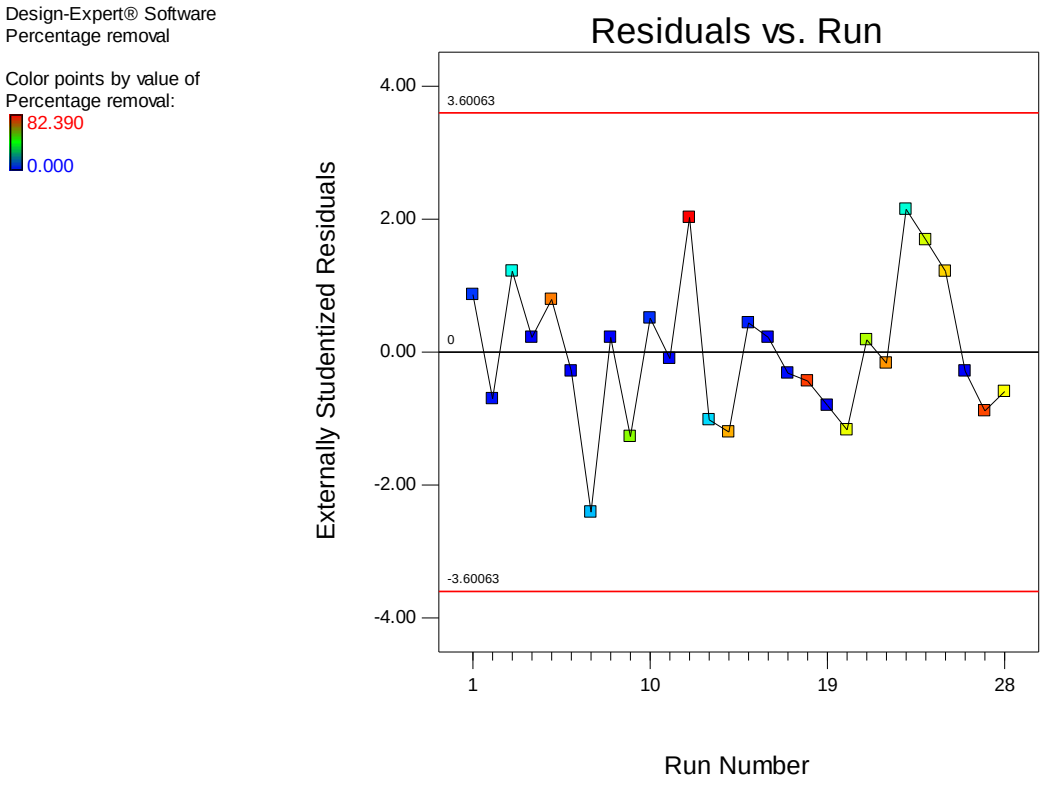

Figure 18: Residuals versus Run Analysis

Design-Expert provides upper and lower red lines that are similar to 95% confidence control limits on a run chart. In this case none of the points stands out. Because this graph is plotted in randomized run order, the ordering of the points on the screen will be different than shown here. Normally, patterns should be looked out for, not just outliers. An obvious example would be a steady decrease in residuals from start to finish, in other words, a downward trend. That would be cause for concern about the stability of the system and merit investigation. However, by running the experiment in random order, there is protection against trends in response biasing the results.

4.3.6 Contour Plots

4.3.6.1 Adsorbent dose-pH Contour Plots

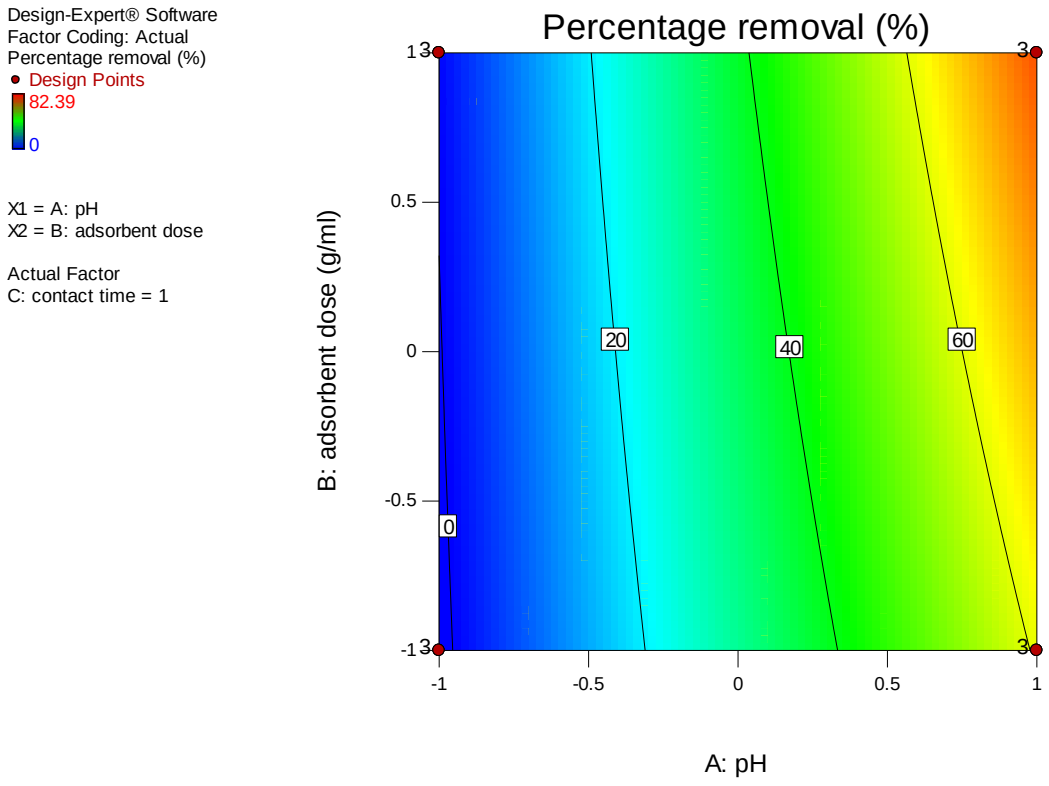

Figure 19: Adsorbent dose-pH Contour Plots

The contour plot for adsorbent dose and pH portray that a higher percentage of removal can be obtained with a high adsorbent dose and high pH value. The colour represents the intensity of percentage removal as the factors vary. The values shown were experiments conducted with a controlled variable, contact time value of 12 hours.

4.3.6.2 Contact time-pH Contour Plots

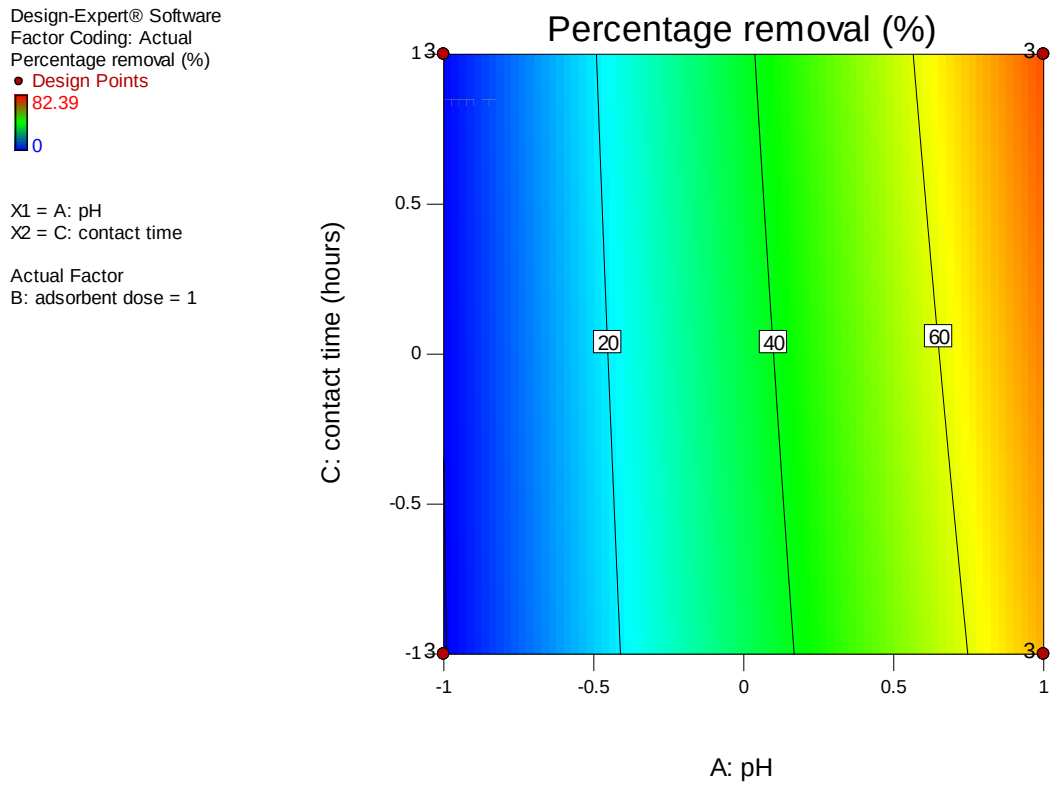

Figure 20: Contact time-pH Contour Plots

The contour plot for contact time and pH portray that a higher percentage of removal can be obtained with a high contact time and high pH value. The colour represents the intensity of percentage removal as the factors vary. The values shown were experiments conducted with a controlled variable, adsorbent dose value of 0.5 g/ml.

4.3.7 Post Analysis

4.3.7.1 Point Prediction

Table 10: Optimal factors

Factor	Name	Level	Low Level	High Level	Std. Dev.	Coding
A	pH	14	6	14	0.000	Actual
B	adsorbent dose	0.5	0.1	0.5	0.000	Actual
C	contact time	12	4	12	0.000	Actual

The values shown in the table above are the parameters that provide the best percentage removal of water hardness.

Table 11: Estimated responses based on parameters in Table 10

	Predicted	Predicted				CI for	Mean	99% of	Population
Response	Mean	Median[1]	Observed	Std Dev	SE Mean	95% CI low	95% CI high	95% TI low	95% TI high
Percentage removal	76.480	76.480	-	6.028	2.978	70.304	82.656	50.634	102.327

The table above describes the outcome of the combination of highest values of parameters. However, the plots tend to show an increasing manner towards the end, indicating that there can still be higher values to be tested that may provide better removal of hardness. The pH value has reached its maximum in this series of experiments and the remaining two factors, adsorbent dose and contact time has shown a minor effect on rate of removal. In order to increase the percentage of removal above 76.48%, different factors need to be considered.

4.4 Adsorption Isotherm

Freundlich and Langmuir isotherm models were used in order to understand the distribution of hardness ions between the liquid phase and solid phase. Figure 21 shows Freundlich isotherm curve where log qe is against log Ce whereas Figure 22 represents Langmuir isotherm curve where Ce (mg/L)/qe (mg/g) is against Ce (mg/L).

Referring to Table 10 below, the R^2 values of Freundlich and Langmuir isotherm models are 0.942 and 0.9566 respectively. Hence, the adsorption process is best described with Langmuir isotherm model as the R^2 value is higher than that of Freundlich isotherm model. Langmuir isotherm model points out that the surface of the adsorbent is homogenous. The degree of nonlinearity between adsorption and solution concentration is signified by the n value and n = 0.369, which means that the adsorption is a chemical process (chemisorption) as $n < 1$. Chemisorption occurs with formation of monolayer of adsorbate on adsorbent.

The K value calculated indicates the maximum uptake of hardness ions by the adsorbent ACSC. Comparing the K values, the K from Langmuir isotherm model is greater than the one of Freundlich isotherm model. In the study, the value of RL obtained is 0.108, which is in between 0 and 1. Thus, the nature of the adsorption is favourable.

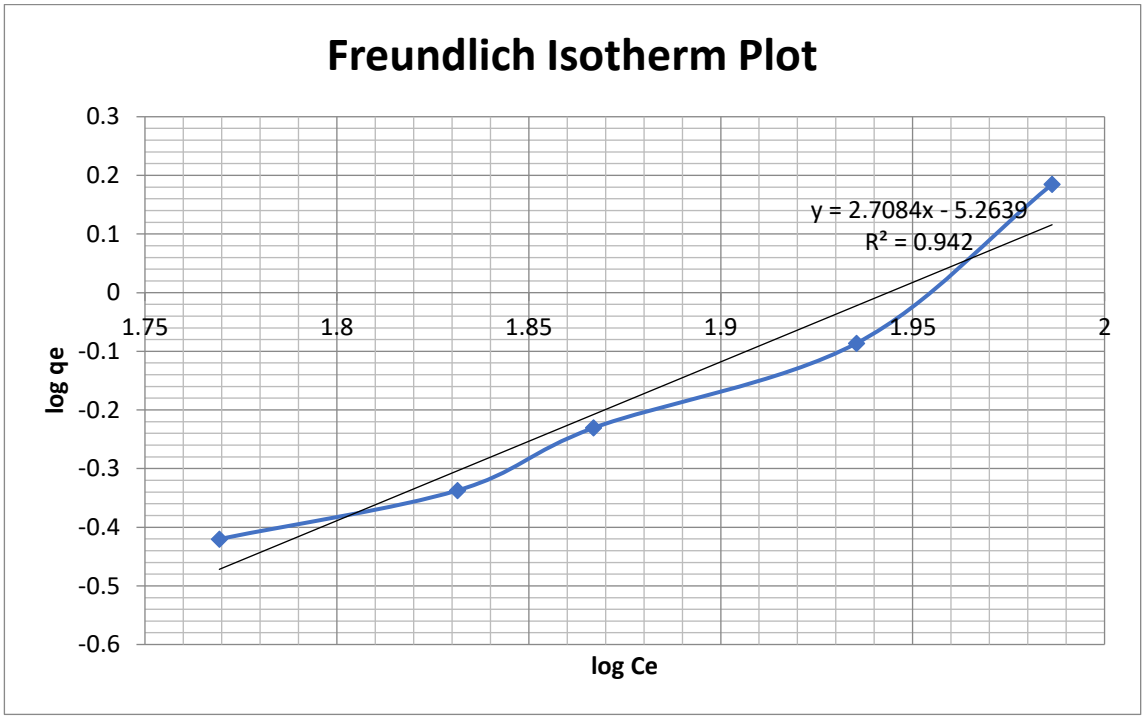

Figure 21: Freundlich Isotherm Plot

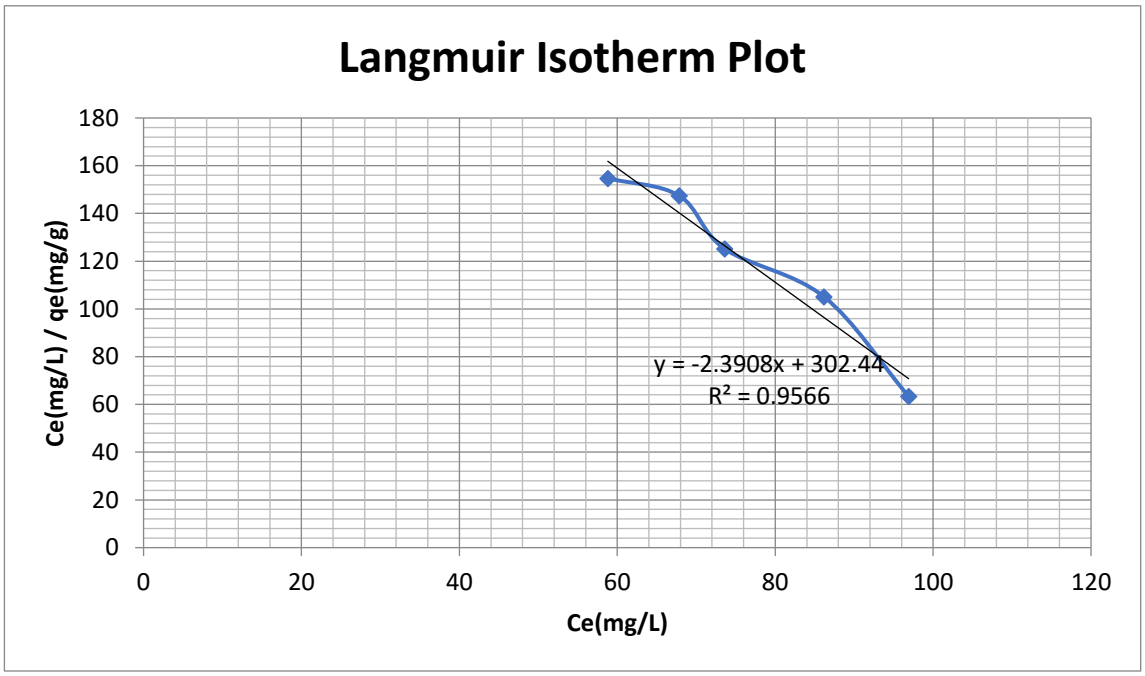

Figure 22: Langmuir Isotherm Plot

Table 12: Isotherm constants for hardness ion adsorption onto ACSC

Adsorbent	Adsorption Isotherm	Isotherm constant	Value
Activated Coconut Shell Carbon (ACSC)	Freundlich	K (mg/g) $(L/mg)^{1/n}$	5.446E-6
		R^2	0.942
		n	0.369
	Langmuir	K (mg/g)	0.418
		b (L/mg)	0.033
		R^2	0.9566
		R_L	0.108

4.5 Kinetic Study

Pseudo-first-order and pseudo-second-order models were used to describe the water hardness adsorption phenomenon on ACSC. By applying Equation 9 and 10, the reaction rate constants for both models were calculated. From Table 12, the R^2 value of pseudo-second-order plot is nearer to the value of 1 and greater than the R^2 value of pseudo-first-order plot. Hence, the pseudo-second-order model is chosen to represent the experiment compared to pseudo-first-order model.

The $q_{e,\ cal}$ of the pseudo-first-order kinetic plot is nearly equal to the $q_{e,\ exp}$ value whereas $q_{e,\ cal}$ of the pseudo-second-order kinetic plot shows a bigger difference from the $q_{e,\ exp}$ value. It is concluded that the adsorption of water hardness by ACSC better expressed with pseudo-first-order kinetic plot rather than pseudo-second-order kinetic plot. Thus, that could clarify the model applicability in this study.

By applying pseudo-first-order model, the reaction follows chemisorption which supports Langmuir isotherm model theory that mentioned the adsorption is a chemical process.

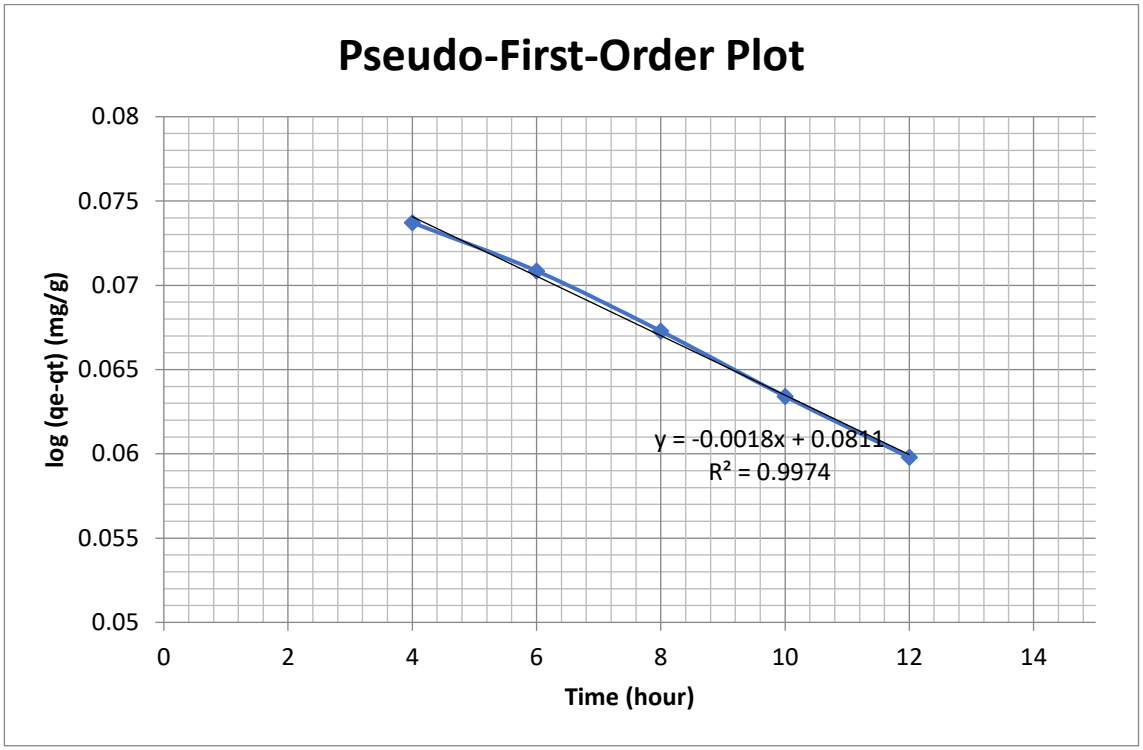

Figure 23: Pseudo-First-Order Plot

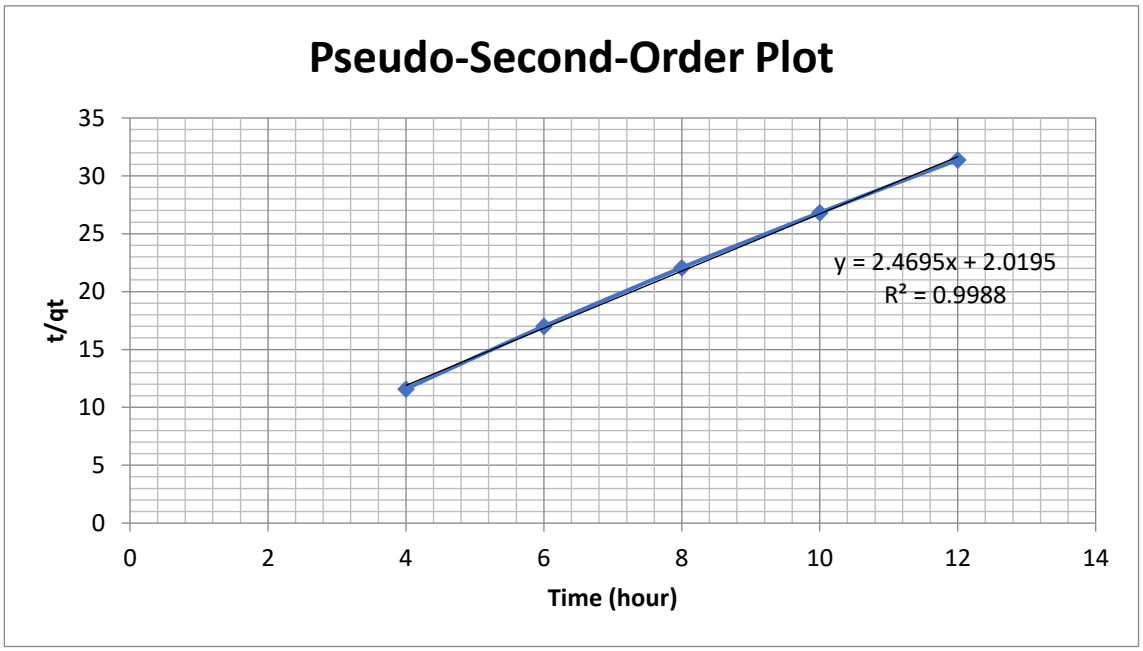

Figure 24: Pseudo-Second-Order Plot

Table 13: Kinetic constants for Ca^{2+} adsorption on ACSC

Adsorbent	qe, exp (mg/g)	Pseudo-First-Order			Pseudo-Second-Order		
		qe, cal (mg/g)	K1 (h-1)	R2	qe, cal (mg/g)	K2 (g/mg.h)	R2
ACSC	1.53	1.205	0.0018	0.9974	0.405	3.02	0.9988

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In conclusion, ACSC possesses stronger –OH and –COOH groups that assist in adsorption of calcium ions when compared to CSC. The higher average pore size in ACSC proves that its surface area is larger and able to react with more molecules at a given time. The results that were run on the Design of Expert software under Full Factorial Design showed that the optimal parameter values for pH, contact time, and adsorbent dose that produced the highest percentage of calcium ion removal, which was 82.36%, were 14, 12 hours, and 0.5 g/mL respectively. Significant curvature in the model was noticed and further research using Central Composite Design may be necessary. Equilibrium isotherms have been analyzed using Langmuir and Freundlich isotherm models, and the chemical reaction favored the Langmuir isotherm model meaning that the adsorption follows a monolayer approach. Kinetic study was conducted using Pseudo-First-Order and Pseudo-Second-Order equations, and it was observed that the chemical reaction suited the Pseudo-Second-Order model showing that the adsorption process was a chemical process.

5.2 Recommendations

There are a few recommendations applicable for this study. For example, in the activation stage, the coconut shell granules can be impregnated with different chemical

agents such as sulfuric acid (H_2SO_4), or potassium hydroxide (KOH). KOH causes widening of micropore width while H_3PO_4 leads to a more heterogeneous pore size distribution [18].

Apart from that, coconut shell carbon can be activated through chemical-physical activation. The carbon will first be chemically activated with $ZnCl_2$, followed by physical activation using steam. Since $ZnCl_2$ acts as a dehydrating agent, the chemical activation of carbon using it tends to produce a high carbon yield, allowing more carbon to be kept fixed. As a benefit for this high yield, the porosity may continue to be further developed by physical activation.

Lastly, for further study, column testing can be conducted after completing the batch experiments. The activated carbon will be placed in a vertical column set-up while hard water sample is continuously flowing through it. This is to study the ACSC hardness ions removal efficiency and performance under a continuous flow.

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APPENDICES

Diagnose Case Statistics

					Internally	Externally		Influence on	
Run	**Actual**	**Predicted**			**Studentized**	**Studentized**	**Cook's**	**Fitted Value**	**Standard**
Order	**Value**	**Value**	**Residual**	**Leverage**	**Residual**	**Residual**	**Distance**	**DFFITS**	**Order**
1	4.53	0.72	3.81	0.244	0.726	0.718	0.028	0.408	21
2	1.27	0.72	0.55	0.244	0.104	0.102	0.001	0.058	20
3	22.33	31.92	-9.59	0.036	-1.621	-1.687	0.016	-0.325	26
4	0.000	-2.48	2.48	0.244	0.473	0.465	0.012	0.264	1
5	72.40	68.74	3.66	0.244	0.699	0.690	0.026	0.392	10
6	0.000	-1.41	1.41	0.244	0.269	0.263	0.004	0.150	13
7	15.37	31.92	-16.55	0.036	-2.796	-3.403	0.048	-0.655	28
8	0.000	-2.48	2.48	0.244	0.473	0.465	0.012	0.264	2
9	52.40	52.97	-0.57	0.244	-0.108	-0.106	0.001	-0.060	6
10	3.81	0.72	3.09	0.244	0.589	0.580	0.019	0.330	19
11	0.40	-1.41	1.81	0.244	0.346	0.338	0.006	0.192	14
12	82.39	76.48	5.91	0.244	1.128	1.135	0.068	0.645	24
13	17.75	31.92	-14.17	0.036	-2.394	-2.720	0.035	-0.524	25
14	68.30	68.74	-0.44	0.244	-0.084	-0.082	0.000	-0.046	11
15	2.59	-0.35	2.94	0.244	0.560	0.552	0.017	0.313	8
16	0.000	-2.48	2.48	0.244	0.473	0.465	0.012	0.264	3
17	1.00	-0.35	1.35	0.244	0.257	0.252	0.004	0.143	7
18	77.58	76.48	1.10	0.244	0.210	0.205	0.002	0.117	22
19	0.000	-0.35	0.35	0.244	0.066	0.065	0.000	0.037	9
20	60.33	60.71	-0.38	0.244	-0.072	-0.071	0.000	-0.040	18
21	55.37	52.97	2.40	0.244	0.459	0.450	0.011	0.256	4
22	70.40	68.74	1.66	0.244	0.317	0.310	0.005	0.176	12
23	23.94	31.92	-7.98	0.036	-1.349	-1.376	0.011	-0.265	27
24	58.32	52.97	5.35	0.244	1.021	1.022	0.056	0.581	5
25	65.20	60.71	4.49	0.244	0.857	0.852	0.040	0.484	17
26	0.000	-1.41	1.41	0.244	0.269	0.263	0.004	0.150	15
27	76.66	76.48	0.18	0.244	0.034	0.034	0.000	0.019	23

28	61.48	60.71	0.77	0.244	0.147	0.144	0.001	0.082	16

Langmuir Isotherm

Co	Ce	Co-Ce	m (g)	qe	Ce/qe
250	96.9	153.1	10	1.53	63.33333
250	86.18	163.82	20	0.82	105.0976
250	73.6	176.4	30	0.588	125.1701
250	67.83	182.17	40	0.46	147.4565
250	58.8	191.2	50	0.38	154.7368

Freundlich Isotherm

Co	Ce	Co-Ce	m (g)	qe	log Ce	log qe
250	96.9	153.1	10	1.53	1.986324	0.184691
250	86.18	163.82	20	0.82	1.935406	-0.08619
250	73.6	176.4	30	0.588	1.866878	-0.23062
250	67.83	182.17	40	0.46	1.831422	-0.33724
250	58.8	191.2	50	0.38	1.769377	-0.42022

Pseudo-First-Order

Time	Co	Ce	Co-Ce	m (g)	qt (mg/g)	qe-qt	log (qe-qt)
4	250	77.5	172.5	50	0.345	1.185	0.0737184
6	250	73.6	176.4	50	0.3528	1.1772	0.0708503
8	250	68.78	181.22	50	0.36244	1.16756	0.0672792
10	250	63.6	186.4	50	0.3728	1.1572	0.0634084
12	250	58.8	191.2	50	0.3824	1.1476	0.0597905

Pseudo-Second-Order

Time	Co	Ce	Co-Ce	m (g)	qt (mg/g)	t/qt
4	250	77.5	172.5	50	0.345	11.5942
6	250	73.6	176.4	50	0.3528	17.0068
8	250	68.78	181.22	50	0.36244	22.07262
10	250	63.6	186.4	50	0.3728	26.82403
12	250	58.8	191.2	50	0.3824	31.38075