Effect of activation condition of biochar on p-nitrophenol adsorption performance

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

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May 2012

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.

SARAH ATIKA BINTI HALIMI

ABSTRACT

Biochar has been used as precursor for activated carbon, using zinc chloride as activating agent. The presence of phenol and phenolic compounds even at low concentration in water and wastewater has been one of the biggest public concern and they are considered to be one of the most frequent contaminants at hazardous-waste sites. Its usage is for removal of p-nitrophenol (PNP). The results of this study show it is feasible to prepare activated carbons with relatively high adsorption performance from biochar by direct chemical activation. From the study it can be seen that biochar that is mixed with 1M concentration of $ZnCl_2$ and activated at 500°C with weight ratio of biochar and $ZnCl_2$ 1:3having the best activation condition as it gives the best adsorption performance by having the highest adsorption capacity which is 703.51mg/g.In this project it is found that adsorption of PNP follows both Freundlich and Langmuir isotherm model with a regression constant almost 0.90.

ACKNOWLEDGMENTS

First, I would like to sincerely acknowledge my supervisor, Prof. Dr. Yoshimitsu Uemura, my deepest gratitude for all your guidance, constructive suggestions and support through my graduate program. Thank you for teaching me on how to become a researcher and for the enormous time, insightful criticisms and patient encouragement aided in the completion of my experiment and writing of this thesis. My gratitude also goes to Ms. Hafizah Afif, I gratefully acknowledge your advice, guidance and for supplying the Biochar used for this project.

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Regards,
Sarah Atika Binti Halimi

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CHAPTER 1

1 INTRODUCTION

1.1 Background

The presence of phenol and phenolic compounds even at low concentration in water and wastewater has been one of the biggest public concern and they are considered to be one of the most frequent contaminants at hazardous-waste sites. p-nitrophenol is a common pollutant found particularly formed due to the photo degradation of pesticides and its compound are present in the effluent of a number of industrial units such as coke ovens in steel plants, petrochemical, oil refineries, phenolic resins, pharmaceutical and other industries (Halif, Daud, Noor, & Hassan, 2007).

The discharge of phenolic waste into waterways may adversely affect human health as well as that of flora and fauna. The toxicity imparted by phenolic compounds is responsible for health hazards and dangerous to aquatic life. Ingestion of a small amount of phenol (5ppm) by human beings may cause nausea, vomiting, paralysis, coma and even death from respiratory failure or cardiac arrests (Alam, Ameem, Muyib, & Kabbashi, 2009). Therefore, removal of phenols from industrial effluents is required before sewage disposal. There are various environment-friendly methods have been suggested. Several physiochemical and biological treatment techniques (solvent extraction, ion exchange by resins, chemical oxidation by ozone, aerobic or anaerobic biodegradation, etc) already exist today, but the most effective and frequently used procedure for phenol removal is adsorption on activated carbon.

Adsorption is a well-known and powerful removal technique for organic compounds from water. Adsorption is the ideal method because it is non-specific and the adequate activated carbon must exhibit a high volume of micropores of a variety of pore size to be able to adsorb a wide range of molecules, coupled with an adequate proportion of meso and macropores to facilitate the access to the micropores (M.Molina-Sabio & Rodriguez-Reinoso, 2004).Using activated carbon as adsorbents for the removal of phenolic compounds is a very common practice (S.Dutta & Ghar, 2001). Activated carbon is the most effective adsorbent for organic contaminants due to its high surface area, low specificity and fast adsorption kinetics. Recently the usage of activated carbon has been broadened to advanced wastewater treatment. In 2006, the average cost of activated carbon from the major producer was close to $2500 per ton, with a world demand expected to expand 5.2% per year through 2012 to 1.2 million tons (P.Girods, et al., 2009)As a result, the demand for activated carbon is increasing. The major constraint of using the carbons in industrial application is high capital and regeneration cost of these activated carbons due to expensive materials used.

There is a scope for developing adsorbents from the low cost material by producing activated carbon from lignocellulosic materials such as agricultural wastes or by-products, coals, wood, fertilizer waste, etc. Lignocellulosic materials are commonly used as the precursor of activated carbon because of two characteristics which are low inorganic materials content and relatively high volatile content (Azargohar & Dalai, 2008).

In the sense of environmental safety, the utilization of these wastes has awakened the interest development of processes for transforming the agricultural residues into a strong influence on the porous structure activated carbon with good adsorption properties and also providing a high quality end product for water and wastewater treatment (Aygun, yenisoy-Karakas, & I.Duman, 2003).Biochar is one of the products of fast pyrolysis including agricultural wastes such as palm kernel shell, sawdust, rice husk, bagasse and wheat straw (Azargohar & Dalai, 2008). Biochar is a carbon-enriched and porous material produced from a variety of biomass that has been pyrolysed in a zero or low oxygen environment. Biomass is similar in its appearance to charcoal, char, activated carbon, and other black carbon materials. Biochars have potential to be used as active filter media for adsorpting pollutants (p-nitrophenol) from wastewaters (Azargohar & Dalai, 2008).

1.2 Problem Statement

Many researchers have studied the activation process and the effects of their operating conditions. However, there is still no study on the effect of activation condition on biochar on p-nitrophenol adsorption performance.

In the present work a low cost adsorbent is developed using biochar as a raw material and its usage is for removal of p-nitrophenol. This is to estimate and to know the applicability of produced activated carbon (biochar) as an adsorbent for wastewater treatment; adsorption performance test has been performed using p-nitrophenol as the adsorbate.

1.3 Objective and Scope of Study

To study the effect of activation conditions of biochar on chemical activation atdifferent temperature, different mass ratio of biochar and $ZnCl_2$ and different concentration of $ZnCl_2$on the adsorption rate and to see the nature of adsorption isotherm of p-nitrophenol.

The effect of activation condition of biochar on p-nitrophenol adsorption performance project is practicable project for my final year project because it is done within this semester.

CHAPTER 2

2 LITERATURE REVIEW

2.1 Activated Carbon

Activated carbon is the carbonaceous material that is very effective adsorbents for organic compounds. Activated carbon is versatile adsorbents. It can be produced from carbonaceous material in order to provide adsorptive properties. The adsorptive properties depend on their high surface area, microporous structure and high degree of surface reactivity. The chemical structure on the carbon surface will influence the interaction between polar and nonpolar adsorbates. Activated carbon can be used to adsorb organic and inorganic species either from gaseous and aqueous phases.

i. Chemical and porous structure of carbon (nature and concentration of surface chemical groups).
ii. The polarity of the surface.
iii. The carbon surface area.
iv. Pore size distribution.
v. Physical and chemical characteristics of adsorbate. (Bansal, 2005)

The porous structure of activated carbon is formed by three types of pores as shown in Figure 1. In this figure, pores are categorized as follows

Micropores: width less than 20 Å

Mesopores: width between 200-500 Å

Macropores: width larger than 500 Å

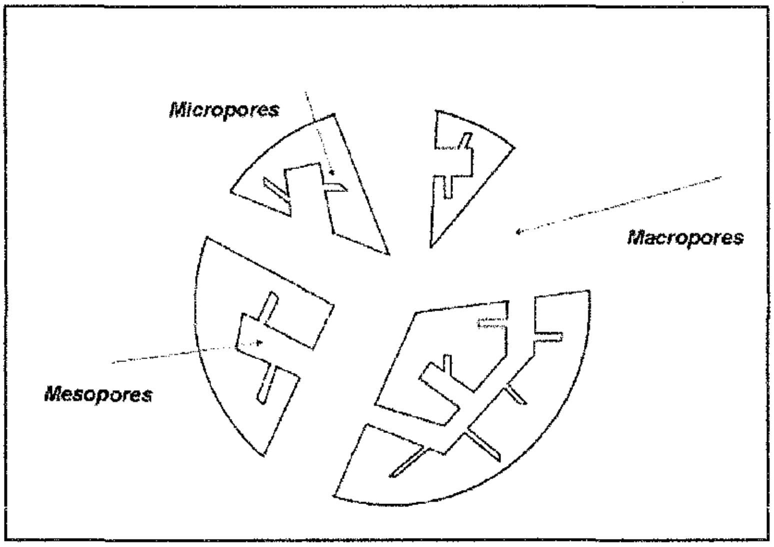


Figure 1: Schematic representation of activated carbon porous structure (Rodriguez-Reinoso & Molina-Sabio, 1998).

Non-graphitic carbon is classified as graphitizable (cokes) and non-graphitizable carbons (chars) (Rodriguez-Reinoso & Molina-Sabio, 1998). Graphitizable carbons can be converted into graphitic carbons by the heat treatment under atmospheric pressure [Marsh, 1991]. Nongraphitizable carbons do not pass through a fluid phase during pyrolysis (carbonization) [Byrne and Marsh, 1995]. These materials are the main precursors for activated carbon. Activated carbons are porous materials with highly developed internal surface area and porosity.

2.2 Application of Activated Carbon

Activated carbon is widely use in industries. Examples of its usage as:

a. Removal of Nitrogen from air.

b. Removal of Hydrogen from syn-gas and hydrogenation process.

c. Recovery of solvent vapors.

d. Removal of SOx and NOx.

e. Purification of helium.

f. Decolorizing of syrups, sugars and molasses.

g. Water purification in removing phenol, halogenated compounds, pesticides, caprolactum and chlorine.

h. Purification of many chemical, food and pharmaceutical products.

i. Air purification in inhabited spaces likes (restaurants and food processing industries).

2.3 Precursors

Activated carbons have been used for a long time as adsorbent in many applications in which impurities in low concentration are removed. It is mainly composed of carbonaceous material with various microporous structure. Its industrial usage can be found in the treatment process for floe gas and volatile solvents,etc. In the treatment of wastewater, it is used for purification, decolorization and the removal of toxic organics and heavy metal ions. Recently, its usage has been broadened to advance wastewater treatment. As a result the demand for activated carbon is increasing (Kim, Myoung-Hoi Sohn, Sohn, & Kwon, 2001).

Activated carbon can be produced from most of carbon containing organic materials, but commercial process to make activated carbon use precursors, which are either of degraded and coalified plant matter or botanical (origin wood, coconut shells and nut shells) (El-Hendawy, 2001)

These materials have high carbon. Previous research has shown that the meso and macroporosity in activated carbon manufactured from lignocellulosic material reflect the botanic texture of the precursor, where areas the microporosity is development along the activation with gases (mainly steam or carbon dioxide), widening the rudimentary porosity of the char. Since variables such as temperature, pressure, heating rate,etc. does not seem to have a significant role in influencing the micropore size distribution, the alternative use of well controlled chemical activation is interesting because the botanic texture of the precursor and the development of porosity is substantially modified (M.Molina-Sabio & Rodriguez-Reinoso, 2004)

Materials from botanical origin or in other word, lignocellulosic materials have low inorganic and relatively high volatile content. The first characteristic results in producing activated carbon with low ash and the second helps to control the production process (Rodriguez-Reinoso, 2002). Biochars have potential to be used as active filter media for adsorpting pollutants (p-nitrophenol) from wastewaters. Biochar has a rudimentary porous structure because of blockage of the pores by tars that caused the internal surface of char is very low, which is insufficient for practical use and has to be enhanced by activation process (Azargohar & Dalai, 2008). Activation is generally carried out in two ways, physical activation and chemical activation.

Table 1: A typical chemical composition of lignocellulosic materials.

Element	Wt (%)
C	48
H	6
O	45
Inorganic Compound	1

2.4 Chemical activation

The chemical activation process is known to be effective for the production of activated carbon used for water and wastewater treatment. Chemical activation of the precursor with a chemical agent is another important industrial process to produce activated carbons and considered as a suitable method for producing highly microporous activated carbon. Chemical activation commonly utilizes chemical such as Zinc Chloride ($ZnCl_2$), Phosphoric Acid (H_3PO_4) and Pottasium hydroxide (KOH). Figure 2 shows the general flow sheet for chemical activation.

Carbonization and activation usually carried out simultaneously in the chemical activation process. The washing step makes the pore structure available and increased specific surface area of the activated carbon. The product undergoing needs to be washed with acid/base and hot water to remove the inorganic matter from the surface (Kim, Sohn, Kim, Sohn, & Kwon, 2001).

Chemical activation of lignocellulosic materials is mainly directed towards the preparation of powdered activated carbons. Since the precursor is finely divided the homogeneity of the mixture with the reagent is ensured. However, if the objective is to prepare granular activated carbon the impregnation step has to be carried out with special care to ensure the intimate contact between the precursor and the reagent.

When a lignocellulosic precursor is activated with increasing concentrations of zinc chloride, phosphoric acid and potassium hydroxide there is a strong development of porosity, initially centred in the microporosity. Consequently, there is a degree of activation, specific for each chemical that develops the maximum volume of micropores without an appreciable contribution from mesoporosity. These values are 0.4 cm3/g for KOH, 0.5 cm3/g for $ZnCl_2$ and 0.6 cm3/g for H_3PO_4.

KOH only produces widening of the microporosity to more heterogeneous micropores, whereas $ZnCl_2$ develops both wide micropores and low mesopores, and H3PO4 also develops large mesopores and even macropores (M.Molina-Sabio & Rodriguez-Reinoso, 2004). The activated carbon produced by $ZnCl_2$ activation are dominantly microporous, but with a significant mesopores which increases by an increase in the impregnation ratio ($ZnCl_2$/precursor) (McEnanney, 2002).

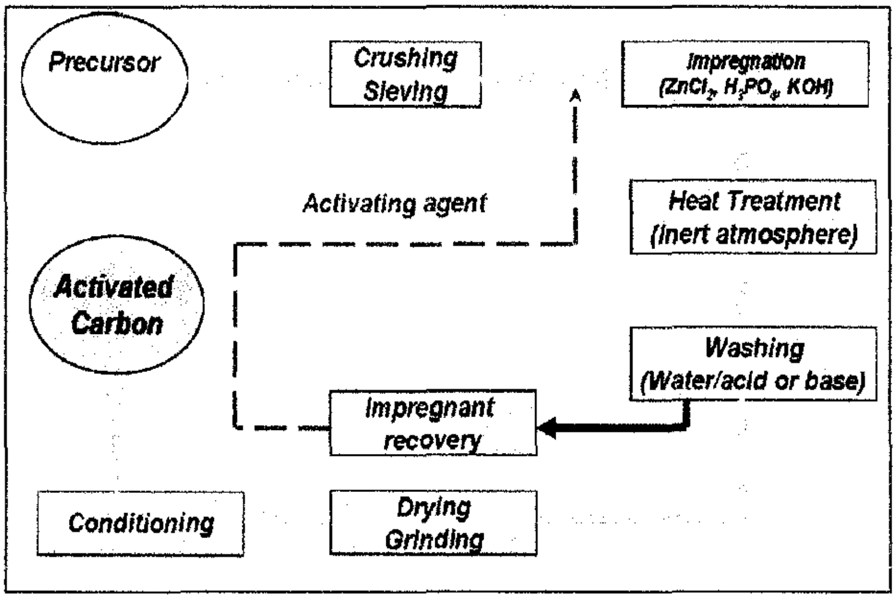


Figure 2: The general flow sheet for chemical activation

The expected result for textural characterization of several activated carbon samples using $ZnCl_2$ as chemical reagent for activation are summarized in Table 1. Data is tabulated for BET area, total pore volume, micropores volume, average pire width, and the ratio of micropores volume to total pore volume (Azevedo, Araujo, Bastos-Neto, B.Torres, Jaguaribe, & Cavalcante, 2007).

Table 2: Textural parameters of the AC samples.

Sample	Precursor amount (g)	$ZnCl_2$/precursor ratio (w/w)	BET area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	Average pore width (Å)	Microporosity (%)
CAQ-29[a]	400	1	1266	0.731	0.676	11.5	92.4
CAQ-30[a]	100	1	1091	0.681	0.549	12.5	80.6
CAQF-29[b]	54[c]		1699	1.003	0.870	11.8	86.7
CAQF-30[b]	36[c]		2114	1.307	1.142	12.4	87.4

[a] CAQ chemical activation only.

[b] CAQF chemical activation with $ZnCl_2$ followed by physical activation.

[c] Precursors for CAQF-29 and CAQF-30 are CAQ-29 and CAQ-30, respectively.

2.5 p-Nitrophenol

4- Nitrophenol, also known as p-Nitrophenol, is a colourless to slight yellow crystalline material with very little odour, moderately toxic pollutant that is moderately soluble in cold water and denser than water. 4-Nitrophenol is produced either by the catalytic hydrolysis of 4- nitrochlorbenzene or by the reaction of dilute HNO_3 on phenol and subsequent steam distillation to separate the 4- from the 2-isomer (HSDB, 1989). It is an important fine chemical intermediate, serving as a precursor for pesticides and pharmaceutical products which had been selected by the EPA (2000) as one of the persistent, bioaccumulative and toxic (PBT) chemicals. The frequent application of this chemical for agriculture, industrial and defense purposes had led to its presence in water bodies. Technologies such as aerobic, anaerobic biodegradation process, advanced oxidation processes and adsorption have been used to remove 4-nitrophenol from domestic and industrial effluents (Karim and Gupta, 2003).

2.6 Adsorption Isotherm

Several models have been used in the literature to describe the experimental data of adsorption isotherms. The Freundlich and Langmuir models are the most frequently employed models. In the present work both models were used.

The p-nitrophenol sorption isotherm followed the linearized Freundlich model as shown in The relation between the metal uptake capacity 'q_e' (mg/g) of adsorbent and the residual metal ion concentration 'C_e' (mg/l) at equilibrium is given by

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e$$

Where the intercept ln *k* is a measure of adsorbent capacity, and the slope 1/*n* is the sorption intensity.

CHAPTER 3

3 METHODOLOGY

3.1 The Research Process

1. Biochar is used as raw material for chemical activation process.
2. Biochar to $ZnCl_2$ mass ratio of 1:1, 1:3 and 1:7
3. Temperature and time is 27°C and 2 h for impregnation biochar with $ZnCl_2$
4. Temperatures of activation process are 400°C and 500°C
5. The amount of adsorbent ranging from 0.05 to 0.2g for adsorption analysis.
6. Concentration of initial PNP solution are 250,350,500,625 and 750 mg/L
7. For phenol analysis, by using UV-visible spectrophotometer, the wavelength used is 318nm.

3.2 Project Activities

3.2.1 Chemical Activation Process

3.2.1.1 Experimental

Raw material biochar is used as starting material. The biochar was produced from palm kernel shell using fast pyrolysis (Figure 3).

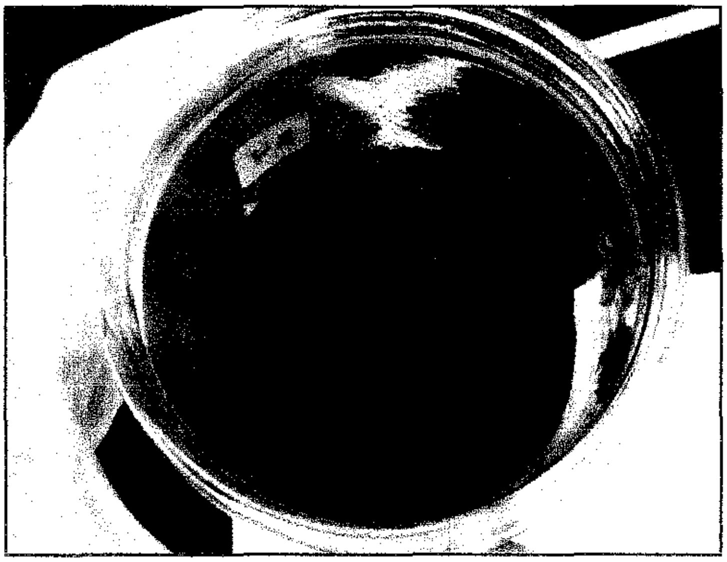


Figure 3:Biochar from palm kernel shell

3.2.1.2 Procedure

Raw material used is biochar for chemical activation process. Specified amount of $ZnCl_2$will be impregnated in biochar. The char is mixed with $ZnCl_2$solution at desired concentration.

This mixture then is kept at the room temperature to ensure the access of $ZnCl_2$ to the interior of the biochar. After two hours, the mixture is dried at 120°C in an oven for 24 hours.

Prepared sample is then be placed in the fixed bed reactor under a nitrogen flow, which is heated to 300°C at 3°C/min and remain with this temperature for 1 hour to prevent carbon loss through direct attack of steam. Then the temperature will be increase at the same heating rate to reach the desired temperature. The chemical activation will be carried out for 2 hours at this temperature before cooling down.

Then the product will thoroughly wash with water, followed by 0.1M HCL, and finally by distilled water to remove the soluble salts. Lastly, the sample will be dried at 110°C for 12 hours (Azargohar & Dalai, 2008).

3.2.1.3 Design of experiment

Three parameters have been varied:

- Activation temperature, 400°C and 500°C
- Concentration of activating agent 1, and 5M
- Mass ratio of raw material and $ZnCl_2$ 1:1, 1:3 and 1:7

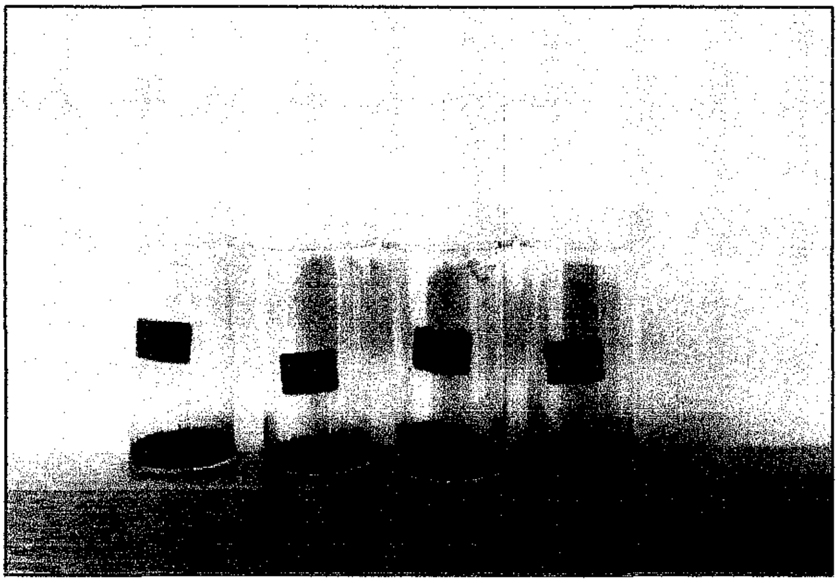


Figure 4:Activated biochar at different mass ratio of raw material and $ZnCl_2$

3.2.2 Adsorption Measurement

PNP solution is prepared in non buffled distilled water in the concentration range of 250-750mg/L.Then, mix calculated weight of for each concentration activated biochar with 50mL of PNP solution of the desired concentration. Shake the samples mildly and do sampling daily and determine concentration of PNP compound remaining in solution using UV spectrophotometer for analysis.(Petrova, Tsyntsarki, Budinova, Petrov, Velasco, & O.Ania, 2011).

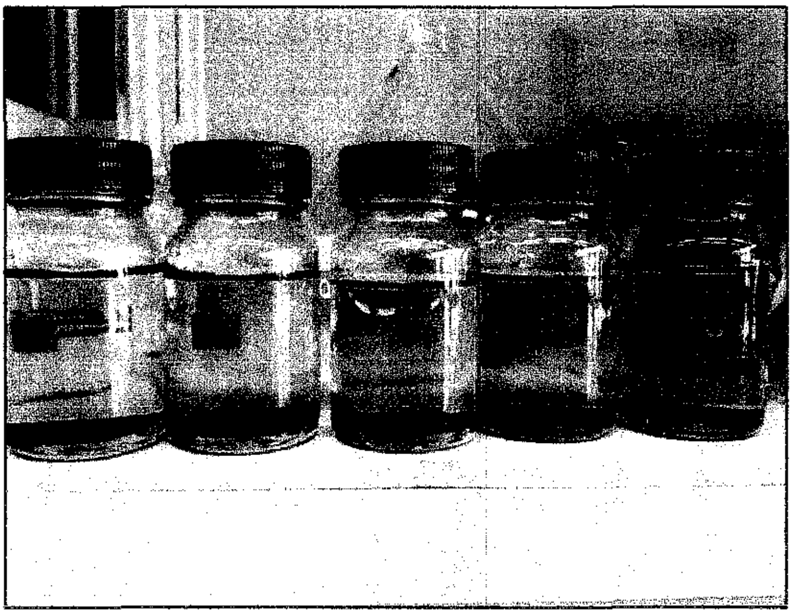


Figure 5: Activated biochar are mixed with PNP solution for adsorption experiment

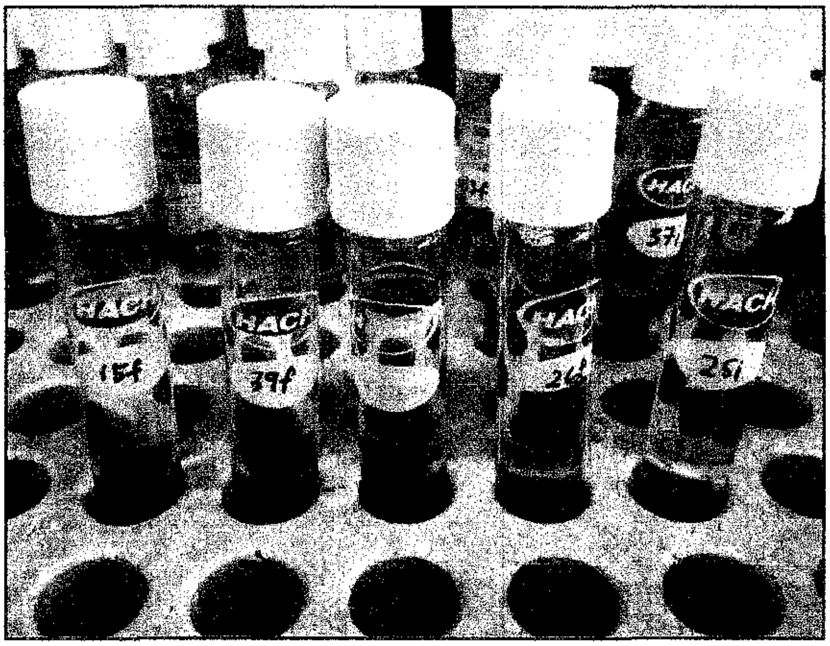


Figure 6: Diluted concentration of PNP to be analysed by UV-Vis spectrophotometer

3.2.3 Data Processing Methods

1) Prepare a calibration curve by plotting absorbance against concentration PNP

    a. Eight standards of known concentration that cover the expected range of the test are prepared.
    b. Customary volume of each known solution is poured into a separate clean sample cell of UV-vis spectrophotometer in block 4.
    c. 318nm of wavelength is selected. Absorbance of the known solutions are recorded and measured.

2) Determine PNP concentration using developed calibration curve.

3) Calculate adsorption capacity, q

The amount adsorbed (q_e) per unit mass of adsorbent will be evaluated from the equation:

$$q_e = V (C_0 - C_e)/m$$

V (ml) = volume of the solution, M (g) = mass of the adsorbent, C_0 (mg/L) = initial concentrations of the aromatic compound in the liquid phase, C_e (mg/L) = equilibrium concentrations of the aromatic compound in the liquid phase

4) Calculate accumulated adsorption capacity, Δq.

5) Repeat step 2-4 for all samples

6) Compare the adsorption performance between the samples

3.3 Tools

1. Activation Unit at Block 5

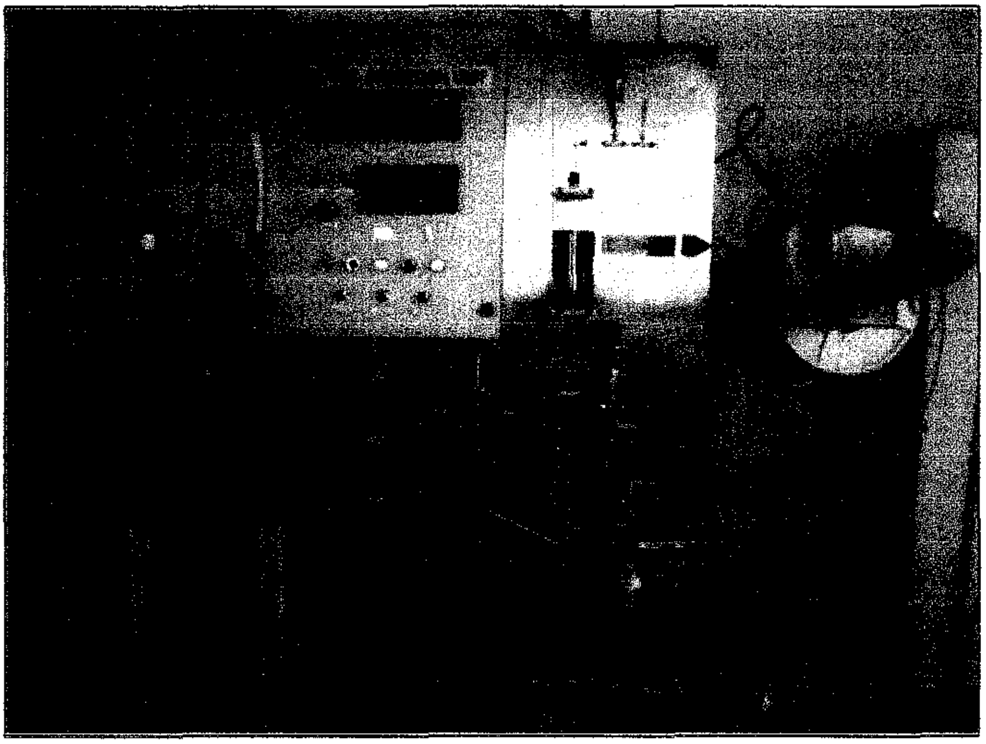


Figure 7: Activation Unit to activated biochar

2. UV Spectrophotometer, Block 4

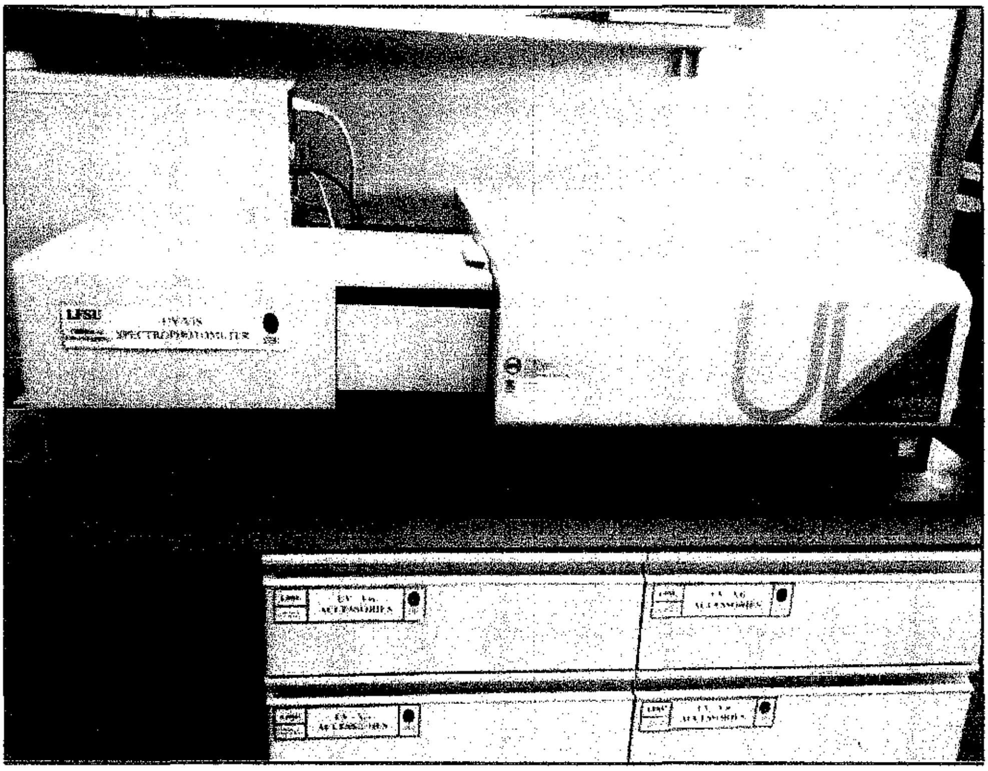
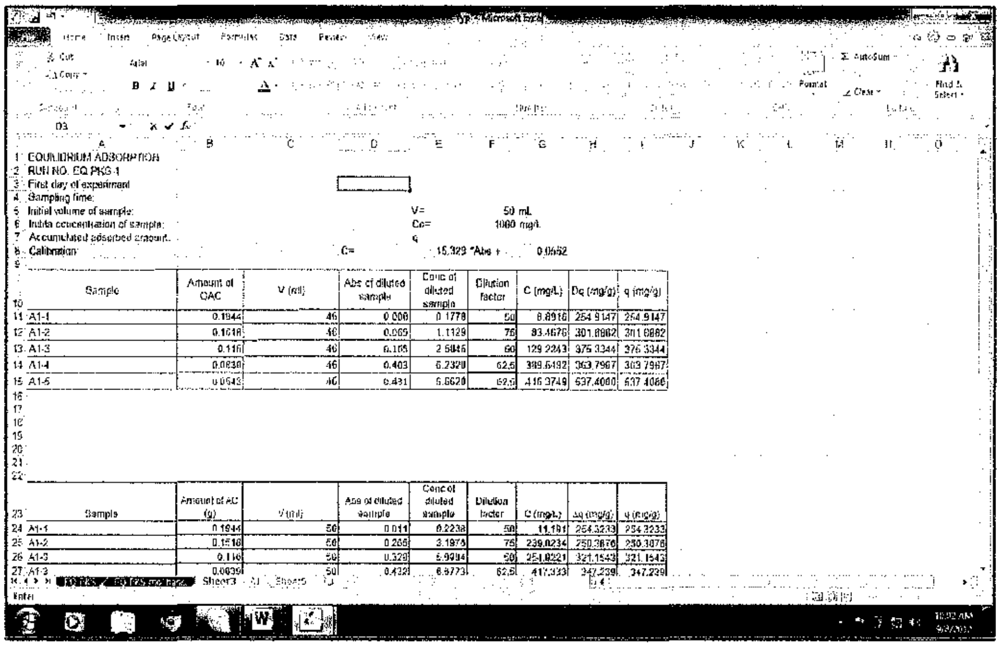


Figure 8:UV-Vis Spectrophotometer used to analysed the concentration of PNP

3. Adsorption calculation using Microsoft Office Excel



EQUILIBRIUM ADSORPTION
RUN NO. EQ PKG 1
First day of experiment
Sampling time:
Initial volume of sample: V= 50 mL
Initial concentration of sample: Co= 1000 mg/L
Accumulated adsorbed amount: q
Calibration: C= 15.329 *Abs + 0.0652

Sample	Amount of OAC	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g)
A1-1	0.1944	46	0.006	0.1778	50	8.8916	254.9147	254.9147
A1-2	0.1618	46	0.069	1.1129	75	83.4676	301.8862	301.8862
A1-3	0.116	46	0.165	2.5846	50	129.2243	375.3344	375.3344
A1-4	0.0830	46	0.403	6.2320	62.5	389.5492	363.7967	363.7967
A1-5	0.0543	46	0.431	6.6620	62.5	416.3749	537.4060	537.4060

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Δq (mg/g)	q (mg/g)
A1-1	0.1944	50	0.011	0.2238	50	11.191	254.3233	254.3233
A1-2	0.1516	50	0.266	3.1976	75	239.0234	250.3876	250.3876
A1-3	0.116	50	0.329	5.9994	50	251.8221	321.1543	321.1543
A1-3	0.0839	50	0.432	6.6773	62.5	417.333	347.239	347.229

Figure 9: Spreadsheet to calculate adsorption capacity

3.4 Project Timeline (Key milestone/ Gantt Chart)

Gantt chart for the project is prepared in order to illustrate the project schedule and important key milestone. The chart is shown in Table 3:

Table 3: Gantt Chart for Final Year Project 2.

No	Detail\Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Activation Process	▨	▨						Mid-semester Break								
2	Characterization procedure and Adsorption test		▨	▨	▨	▨	▨	▨									
3	Progress Report submission									◈							
4	Analyzation of Results				▨	▨	▨	▨		▨	▨	▨					
5	Pre-EDX												◈				
7	Submission of Draft Report													◈			
8	Submission of Dissertation													◈			
9	Submission of Technical Paper														◈		
10	Oral Presentation															◈	
11	Submission of Hardbound Dissertation																◈

Legend	
◈	Suggested milestone
▨	Process

CHAPTER 4

4 RESULT AND DISCUSSION

This part will discuss in more detail on the results the project has gained. After activated the char according to three different conditions, the activated char are then been proceeded for adsorption tests on PNP. Six selected samples of activated char involved, labelled as A1, A3, B1, B3, C2 and C3.

Table 4: Type of activated biochar

Sample Name	Characteristics
A1	Biochar that is activated at 1M concentration of $ZnCl_2$ at 400°C with mass ratio of char and ZnCl2 1:1
A3	Biochar that is activated at 5M concentration of $ZnCl_2$ at 400°C with mass ratio of char and ZnCl2 1:1
B1	Biochar that is activated at 1M concentration of $ZnCl_2$ at 400°C with mass ratio of char and ZnCl2 1:3
B3	Biochar that is activated at 1M concentration of $ZnCl_2$ at 400°C with mass ratio of char and ZnCl2 1:7
C2	Biochar that is activated at 1M concentration of $ZnCl_2$ at 500°C with mass ratio of char and ZnCl2 1:3
C3	Biochar that is activated at 1M concentration of $ZnCl_2$ at 500°C with mass ratio of char and ZnCl2 1:7

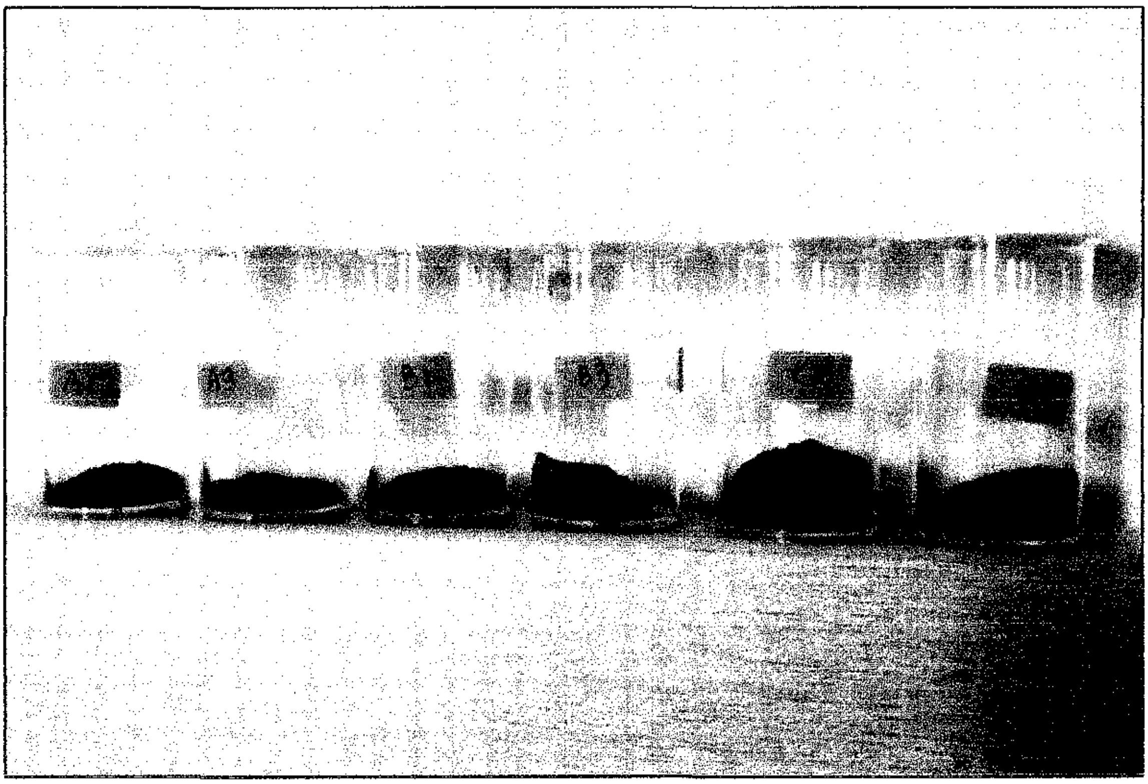


Figure 10: Activated biochar samples used as adsorbent for adsorption experiment

Adsorption experiments were conducted to investigate the rate constants of adsorption for PNP onto activated biochar. The amounts of adsorbates removed by activated biochar were also evaluated in these studies, while the theoretical adsorption capacities of the biochar at all final concentration of PNP in aqueous solution were calculated using Freundlich constants. The equilibrium constant for the Freundlich model were determined from experimental data in table 4.

Below are the adsorption capacity results for sample C2 for 12 days. A1, A3, B1, B3 and C3 results are attached in Appendix 1,2,3,4 and 5.

Initial volume of sample, V = 50ml

Initial concentration of sample, C_0 = 1000 mg/L

Table 5: Result of adsorption experiment on sample C2

Day 2 Wednesday, 11 July 10:00 AM

Sample	Amount of GAC	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g)
C2-1	0.19	50	0.02	0.38	50	18.86	252.35	252.35
C2-2	0.15	50	0.11	1.76	75	131.75	285.98	285.98
C2-3	0.12	50	0.29	4.53	50	226.56	333.38	333.38
C2-4	0.08	50	0.31	4.87	62.5	304.28	414.61	414.61
C2-5	0.05	50	0.48	7.44	62.5	465.24	492.42	492.42

Day 3 Thursday, 12 July 10:15 AM

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g)
C2-1	0.19	48	0.01	0.21	50	10.42	2.08	254.43
C2-2	0.15	48	0.06	0.97	75	73.12	18.54	304.52
C2-3	0.12	48	0.16	2.51	50	125.39	41.86	375.24
C2-4	0.08	48	0.31	4.78	62.5	298.53	3.29	417.9
C2-5	0.05	48	0.25	3.86	62.5	241.05	198.18	690.59

Day 10 Wednesday, 18 July 9:00 AM

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g)
C2-1	0.19	46	0.01	0.15	50	7.36	0.73	255.16
C2-2	0.15	46	0.1	1.65	75	123.71	-15.33	289.19
C2-3	0.12	46	0.15	2.31	50	115.43	3.95	379.19
C2-4	0.08	46	0.27	4.26	62.5	265.96	17.86	435.76
C2-5	0.05	46	0.23	3.64	62.5	227.64	11.36	701.95

Day 12 Friday, 20 July 9.45 AM

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g)
C2-1	0.19	44	-0.01	-0.02	50	-1.07	1.91	257.07
C2-2	0.15	44	0.1	1.53	75	114.51	2.67	291.86
C2-3	0.12	44	0.14	2.14	50	107	3.2	382.39
C2-4	0.08	44	0.27	4.21	62.5	263.08	1.51	437.27
C2-5	0.05	44	0.23	3.61	62.5	225.72	1.55	703.51

Figure 11 below is used to get concentration of p-nitrophenol

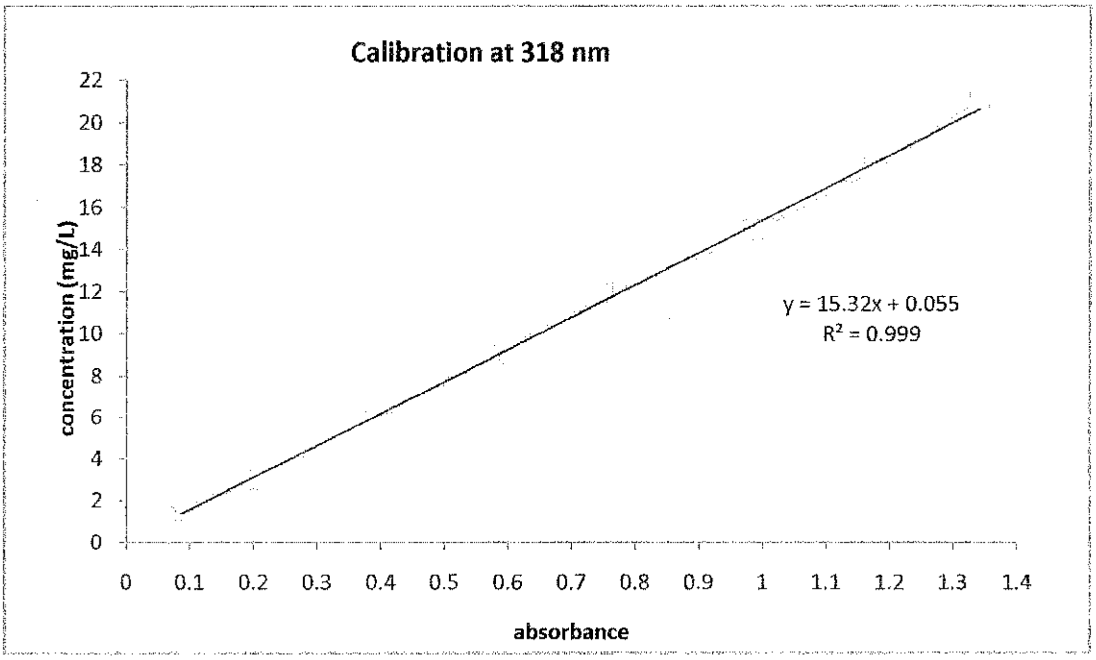


Figure 11: Calibration curve for PNP solution

4.1 Example of calculation for sample C2-5

Adsorption capacity for day 2

$q = (C_o - C_1)(V_o) / m$

$q = (1000 - 465.24)(0.050) / 0.0543$

$q = 492.42$mg/g

Adsorption capacity for day 3

$\Delta q = (C_1 - C_2)(V_1) / m$

$\Delta q = (465.24 - 241.05)(0.048) / 0.0543$

$= 198.18$

So, the adsorption capacity of sample A1-5 for day 3 is

$q = q$ of day $2 + \Delta q$

$q = 492.42 + 198.18$

$= 690.6$ mg/g

4.2 Effect of Contact Time

Figure 12 presents the result for the effect of contact time on the removal of PNP from aqueous solution. It can be seen that the amount of all adsorbates adsorbed onto all six samples of different activation condition of biochar increase with time. For sample C2, about 39.6% PNP had been removed within the third and second day of experiment. This is because of the large surface vacancy existing on the surface of the biochar that are accessible for adsorption during the early stage of experiment. Figure 12 shows the profile for the adsorbates is a single and continuos curve. After day 10, the profile shows small increasing of adsorption capacity due to the non-availability of more vacant site for adsorption onto the biochar.

Figure 13 shows that the concentration of PNP decrease with time. For sample C2, concentrations PNP for day 2 decreased from 465.24mg/L to 241.05mg/L on day 3. This shows about 48.17% of reduction. This proves that the results of this project followed the nature of adsorption.

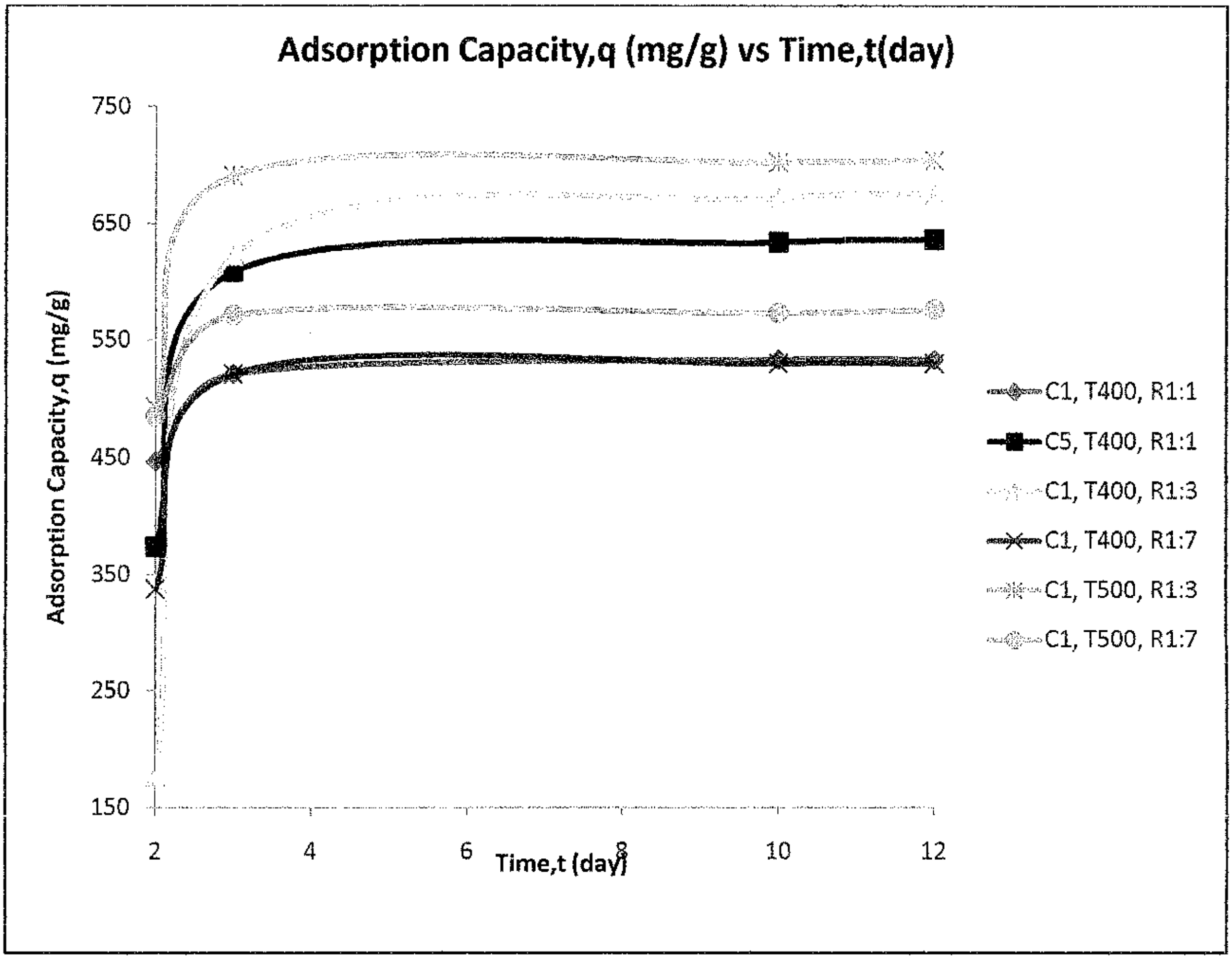


Figure 12: Adsorption capacity,q (mg/g) versus Time (day)

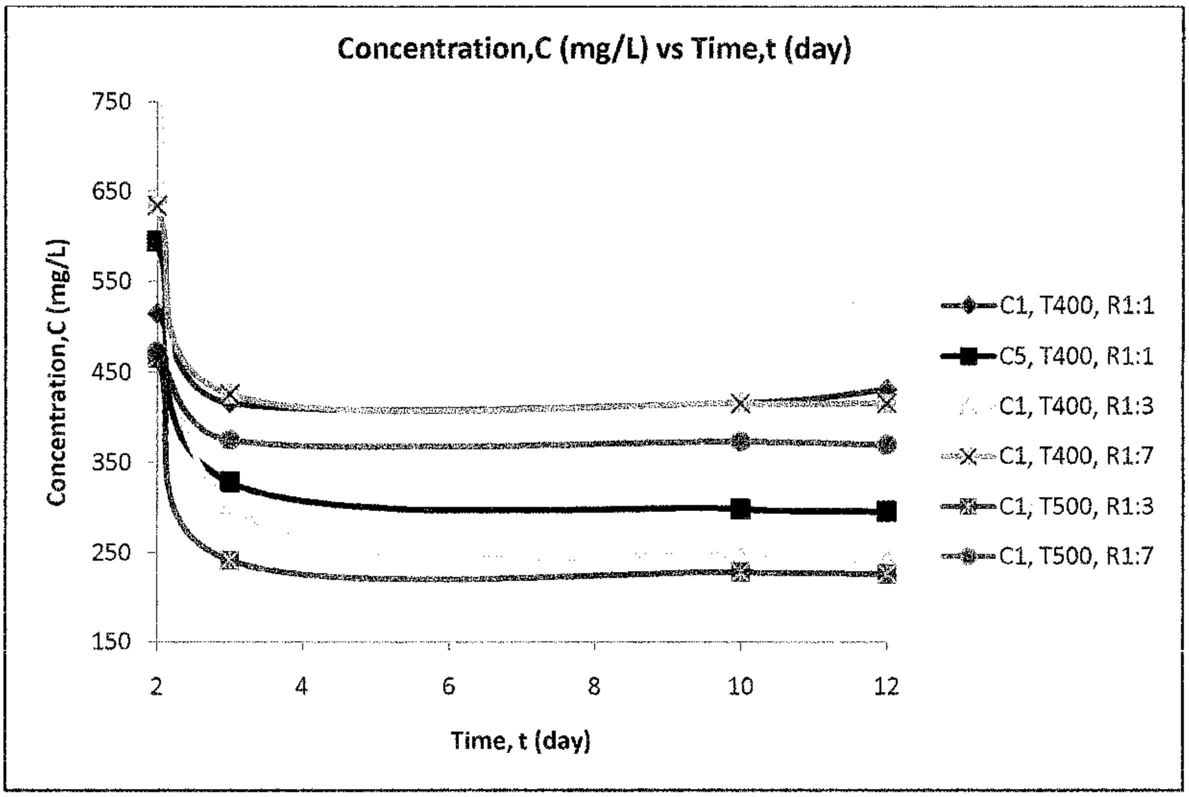


Figure 13: Concentration (mg/L) versus Time (day)

The adsorption capacity increases with the increase in contact time and the adsorption equilibrium reached values as high as 533.24 mg/g, 636.25 mg/g, 674.68mg/g, 529.86 mg/g, 703.51 mg/g and 576.47mg/g for sample A1, A3, B1, B3, C2 and C3 respectively after 12 days of experiment.

Sample C2 is biochar that is mixed with 1M concentration of $ZnCl_2$ and activated at 500°C with weight ratio of biochar and $ZnCl_2$ 1:3having the best activation condition as it gave the best adsorption performance by having the highest adsorption capacity which is 703.51mg/g. The final adsorption capacities for all samples which are activated at different methods are plotted in Figure14.

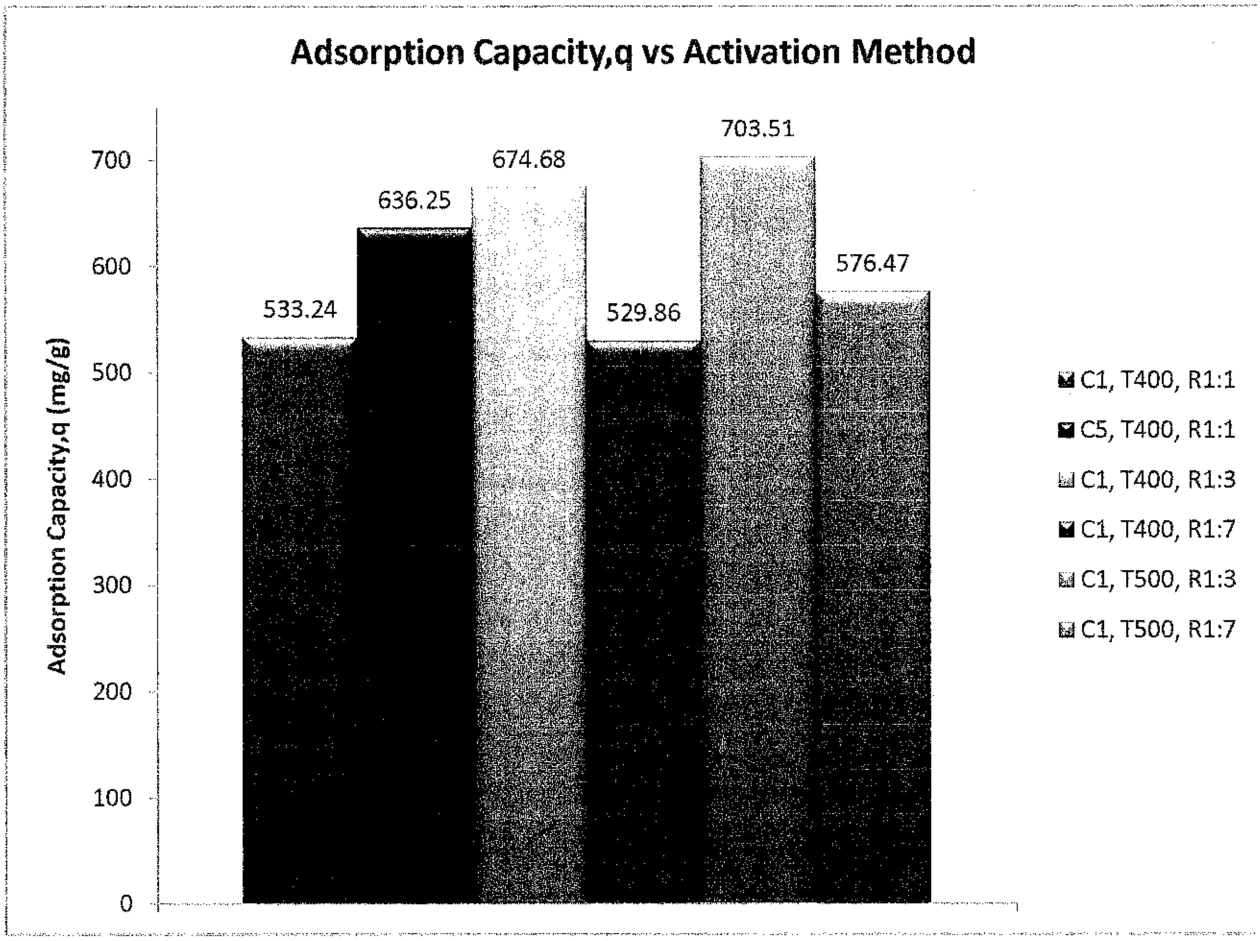


Figure 14: Adsorption capacity,q (mg/g) versus Activation Methods

4.3 Effect of the concentration of activating agent on adsorption performance

The impregnation process was carried on with two different concentrations of $ZnCl_2$ which are 1M (sample A1)and 5M (sample A3) but identical activation temperature and mass ratio of biochar and $ZnCl_2$. The adsorption performance by sample A3 gave higher rate than sample A1 with a value of 636.25 mg/g. Concentration of 1M gave low adsorption rate because of insufficient $ZnCl_2$ to react with the biochar to capably create the internal pore structures.

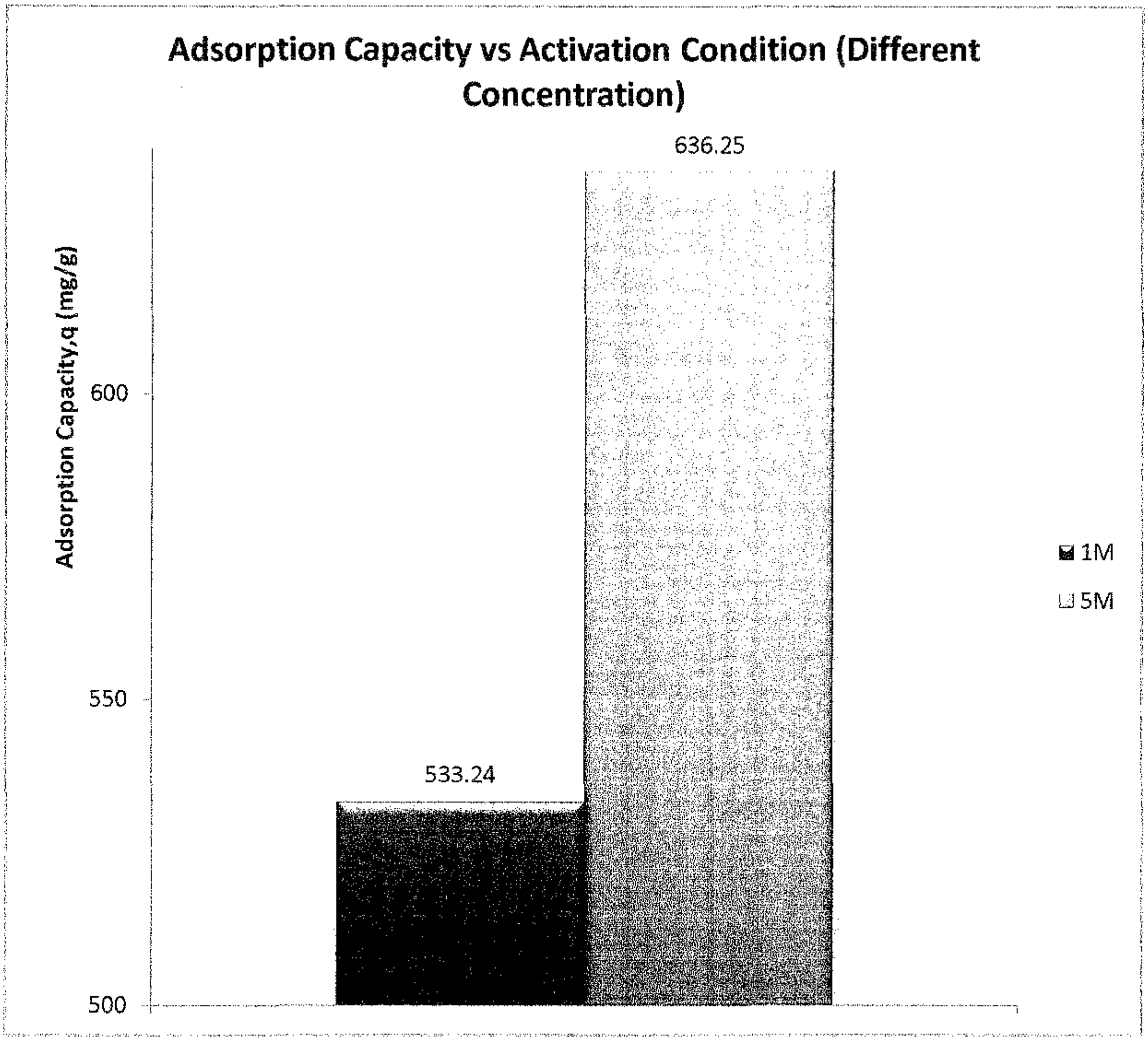


Figure 15: Adsorption capacity of different concentration of ZnCl2 used (1M and 5M)

4.4 Effect of activation temperature on adsorption performance

One of the influential parameter on the pore structure of activated carbon is activation temperature. Two samples were activated at different temperature which named as B1 (400°C) and C2 (500°C) but having the same impregnation process of concentration of $ZnCl_2$ and mass ratio of biochar and $ZnCl_2$. Adsorption capacity increases from 674.68mg/g to 703.51mg/g as temperature increased from 400°C to 500°C due to elevated release of volatile matters during carbonization with temperature increase.

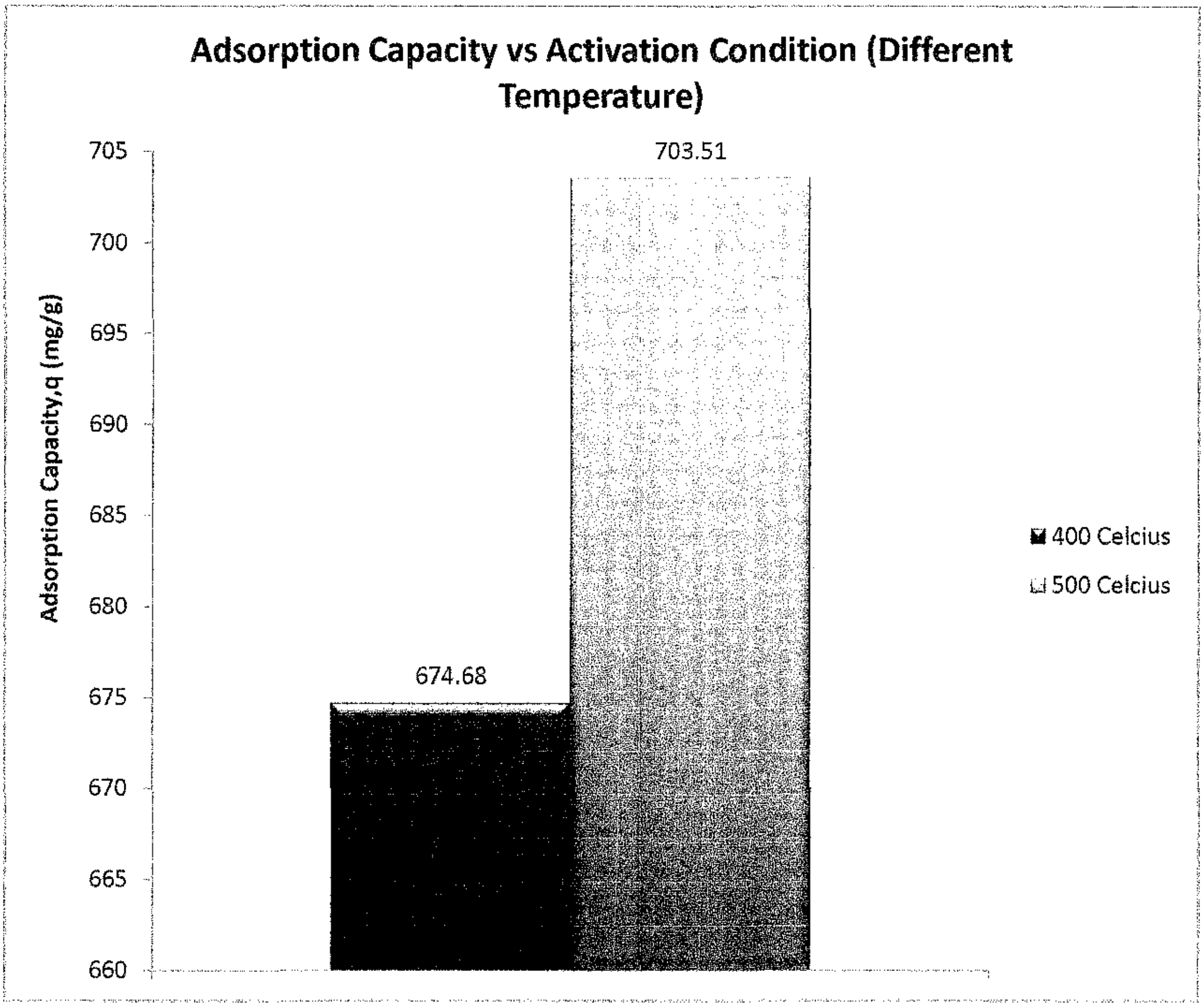


Figure 16: Adsorption capacity of biochar that activated at different temperature

4.5 Effect impregnation mass ratio of biochar and $ZnCl_2$ on adsorption performance

Impregnation mass ratio of raw material and activating agent also plays a big influence in adsorption performance of biochar. Moderate of mass ratio of biochar and $ZnCl_2$ gives best adsorption capacity with value of 674.65 mg/g. Figure 18 shows that mass ratio of biochar and $ZnCl_2$ 1:1 and 1:7 give low result of adsorption rate. This is because high mass of $ZnCl_2$ solution could damage the skin covering the pore structure while too low of $ZnCl_2$will make insufficient $ZnCl_2$ to react with the biochar to capably create the internal pore structures.

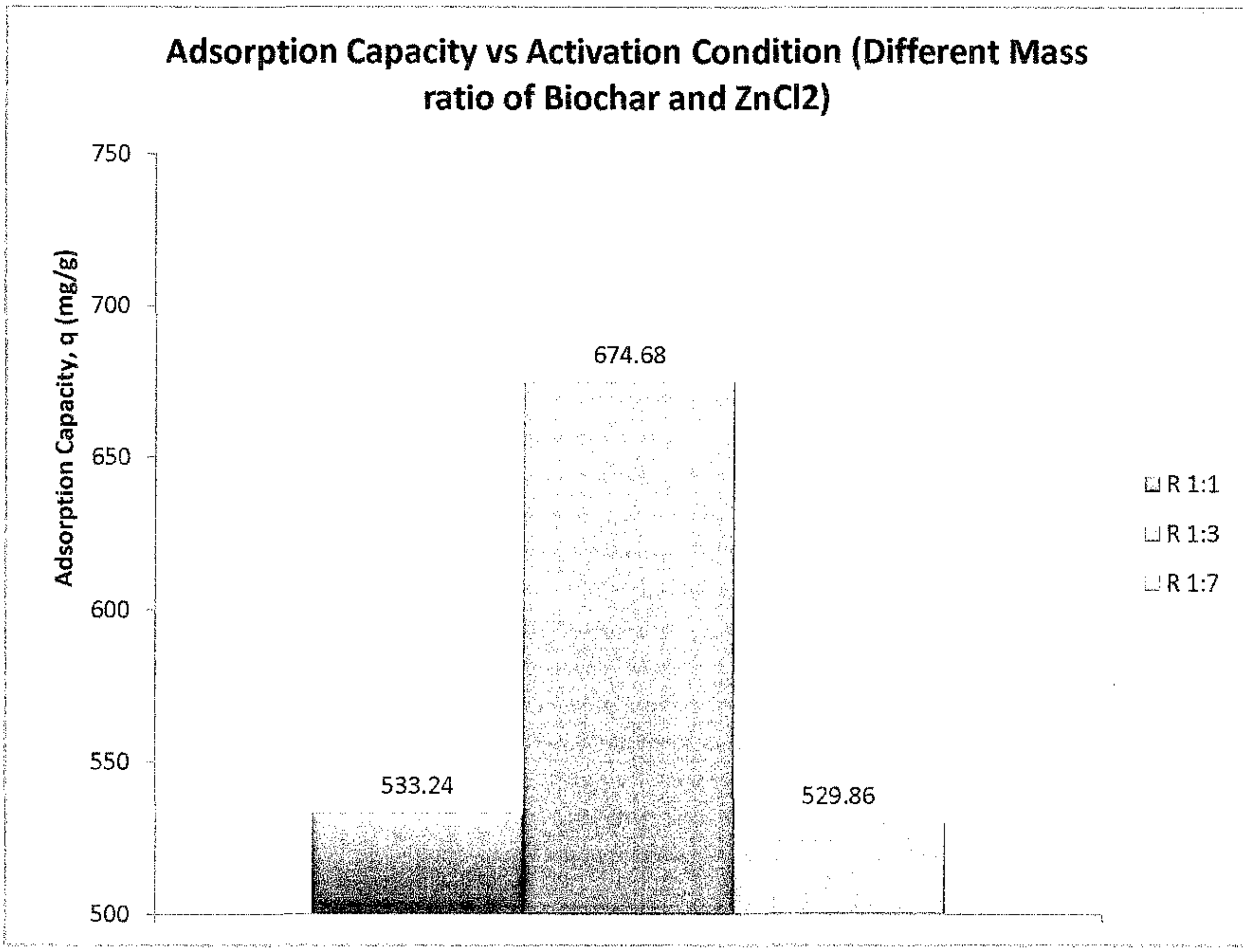


Figure 17: Adsorption capacity of biochar that mixed with different mass ratio of biochar and $ZnCl_2$

4.6 Application of Adsorption Isotherms

Freundlich and Langmuir isotherms are commonly used to describe the adsorption characteristics of activated carbons utilized in water and wastewater treatment. Therefore, adsorption data of biochar that is mixed with 1M concentration of $ZnCl_2$ and activated at 500°C with weight ratio of biochar and $ZnCl_2$ 1:3 (sample C2) were employed to test Freundlich and Langmuir models in this study since it is the best activated carbon produced in this project.

Adsorption isotherms were obtained and the adsorptive capacity interpreted using both models:

$$\text{Log}\,Q = \log K + {}^{1}/_{n} \log C_e$$

The parameter fK and $1/n$ were obtained by linearly regressing each set of experimental data using the equation above.

$$\frac{1}{Q}=\frac{1}{Q_m}+\left(\frac{1}{bQ_m}\right)\left(\frac{1}{C_e}\right)$$

According to the above equation, a plot of 1/Q versus 1/C, should get a straight line. The intercept is $1/Q_m$ and the slope of $1/bQ_m$. These two values will enable one to calculate the two constants for Langmuir model b and Q_m, where the constants are related to the energy of adsorption and capacity, relatively.

Freundlinch and Langmuir adsorption plot of adsorption of PNP on biochar are shown in Figure 18 and Figure 19 respectively. It is seen from the linearity of plots in Figure 18 and Figure 19 that adsorption of PNP follows both Freundlich and Langmuir isotherm model with a regression constat almost 0.90. The value of Freunlinch and Langmuir constants are listed in Table 5. The adsorption capacity K_f and the intensity of adsorption n are calculated from intercept and the slope of freundlinch isotherm plot.

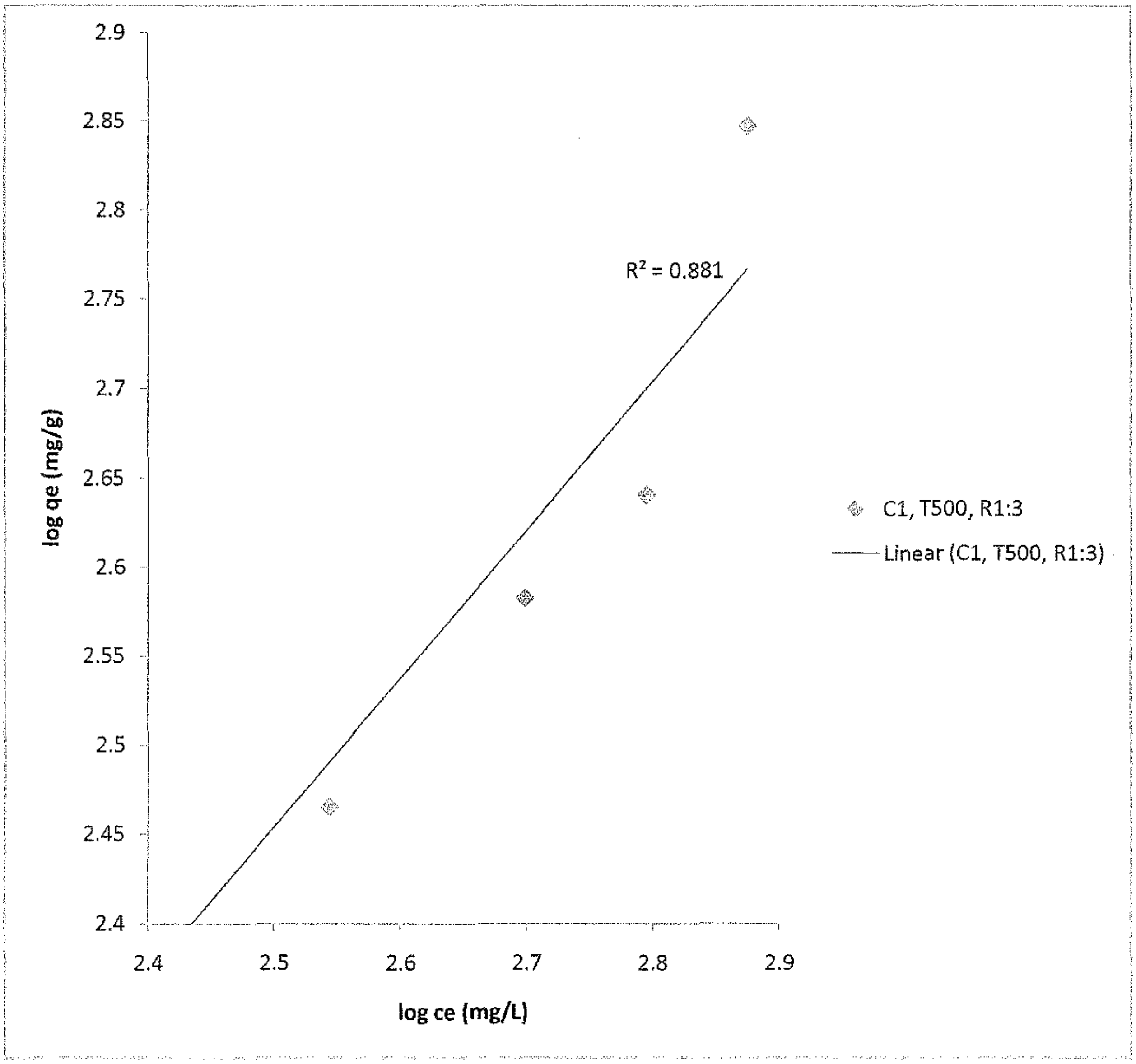


Figure 18: Freundlich plot for adsorption of PNP on biochar (C=1, T=500, R=1:3)

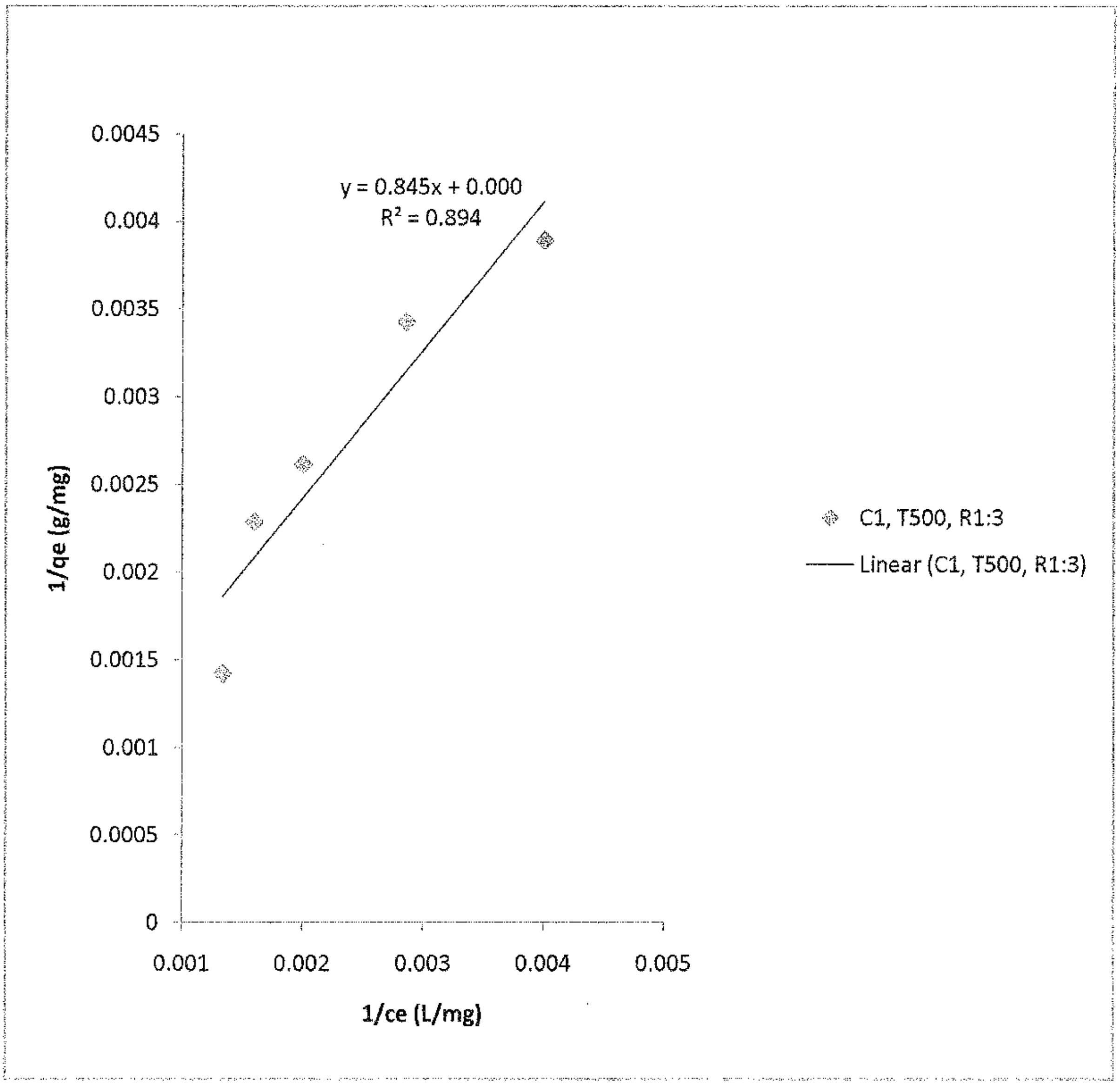


Figure 19: Langmuir plot for adsorption of PNp on biochar (C=1, T=500, R=1:3)

Table 6: Freundlich and Langmuir isotherm constants of adsorption of PNP on biochar

	Langmuir constants			Freundlich constants		
Adsorbent	Q (mg/g)	b	R^2	Kf (mg/g)	1/n	R^2
Biochar	1428.57	0.000828	0.8941	6.809	2.695	0.8896

7.2 APPENDIX 2: Result of adsorption experiment on sample A3 for day 2,3 and 1

Table 8: result of adsorption experiment on sample A3 for day 2,3 and 10

Sample	Amount of GAC	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g)
A3-1	0.1944	50	0.024	0.4231	50	21.1548	251.7606	251.760
A3-2	0.1518	50	0.114	1.8027	75	135.2030	284.8475	284.847
A3-3	0.116	50	0.108	1.7107	50	85.5366	394.1653	394.165
A3-4	0.0839	50	0.416	6.4321	62.5	402.0040	356.3743	356.374
A3-5	0.0543	50	0.617	9.5132	62.5	594.5746	373.3199	373.319

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g)
A3-1	0.1944	48	0.01	0.20849	50	10.4245	2.649457	254.410
A3-2	0.1518	48	0.061	0.990269	75	74.27018	19.26728	304.114
A3-3	0.116	48	0.214	3.335606	50	166.7803	-33.6181	360.547
A3-4	0.0839	48	0.387	5.987523	62.5	374.2202	15.89539	372.269
A3-5	0.0543	48	0.339	5.251731	62.5	328.2332	235.4399	608.759

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g)
A3-1	0.1944	46	0.009	0.1932	50	9.6581	0.1814	254.591
A3-2	0.1518	46	0.053	0.8676	75	65.0728	2.7871	306.901
A3-3	0.116	46	0.214	3.3356	50	166.7803	0.0000	360.547
A3-4	0.0839	46	0.361	5.5890	62.5	349.3106	13.6572	385.926
A3-5	0.0543	46	0.308	4.7765	62.5	298.5333	25.1602	633.920

CHAPTER 5

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

A low cost adsorbent has been developed using biochar as a raw material and its usage is for removal of p-nitrophenol. This is to estimate and to know the applicability of produced activated carbon (biochar) as an adsorbent for wastewater treatment, a adsorption performance test will be perform using p-nitrophenol as the adsorbate.

This project has achieved its objective which is to study the effect of activation condition of biochar of chemical activation of various process parameters on the adsorption rate and the nature of adsorption isotherm of p-nitrophenol.

The three parameters that has been varied for chemical activation that to be studied the effect of activation condition of biochar on p-nitrophenol adsorption performance are activation temperature, 400°C and 500°C, concentration of activating agent 1M and 5M and weight ratio of raw material and $ZnCl_2$ 1:1, 1:3 and 1:7.

The results of this study show it is feasible to prepare activated carbons with relatively high adsorption performance from biochar by direct chemical activation. From the study it can be seen that is biochar that is mixed with 1M concentration of $ZnCl_2$ and activated at 500°C with weight ratio of biochar and $ZnCl_2$ 1:3 having the best activation condition as it gives the best adsorption performance by having the highest adsorption capacity which is 703.51mg/g.

Biochar that mixed with 5M of $ZnCl_2$ gave higher adsorption capacity that biochar that mixed with 1M concentration of $ZnCl_2$ this is due to incapability of lower concentration to create the internal pore structures. Biochar that activated at higer temperature which is 500°C shows higher adsorption rate performance due to release of volatile matters during carbonization. Moderate of weight ratio of biochar and $ZnCl_2$ gives best adsorption capacity with value of 674.65 mg/g. High mass of $ZnCl_2$ solution could damage the skin covering the pore structure.

5.2 Recommendations

It is recommended that more work should be carried out on how to improve the adsorption capability of biochar by subjecting it to physical and chemical treatments in order to increase its specific surface area and to promote the development of micropores within the biochar, as these treatments are known to change adsorption capacity.

Additional parameters can be varied and carried out to see the effects on the adsorption performance therefore can improve its capability to adsorb phenolic compound. Parameters that may be varied are:

a. Different particle size of biochar
b. Activation time
c. Different type of activating agents

CHAPTER 6

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7 APPENDIX

7.1 APPENDIX 1: Result of adsorption experiment on sample A1 for day 2,3 and 1

Table 7: Result of adsorption experiment on sample A1 for day 2,3 and 10

Sample	Amount of GAC	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g
A1-1	0.1944	50	0.08	1.2815	50	64.0760	240.7212	240.721
A1-2	0.1518	50	0.217	3.3816	75	253.6195	245.8434	245.843
A1-3	0.116	50	0.278	4.3167	50	215.8331	338.0030	338.003
A1-4	0.0839	50	0.425	6.5700	62.5	410.6266	351.2357	351.235
A1-5	0.0543	50	0.658	10.1417	62.5	633.8551	337.1500	337.150

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g
A1-1	0.1944	48	0.007	0.162503	50	8.12515	13.81502	254.536
A1-2	0.1518	48	0.133	2.093957	75	157.0468	30.53682	276.380
A1-3	0.116	48	0.201	3.136329	50	156.8165	24.42068	362.423
A1-3	0.0839	48	0.225	3.504225	62.5	219.0141	109.6234	460.859
A1-5	0.0543	48	0.441	6.815289	62.5	425.9556	183.7786	520.928

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g
A1-1	0.1944	46	0.002	0.0859	50	4.2929	0.9068	255.443
A1-2	0.1518	46	0.132	2.0786	75	155.8971	7.3161	283.696
A1-3	0.116	46	0.183	2.8604	50	143.0204	5.4709	367.894
A1-4	0.0839	46	0.217	3.3816	62.5	211.3496	4.2022	465.061
A1-5	0.0543	46	0.43	6.6467	62.5	415.4169	8.9278	529.856

7.3 APPENDIX 3: Result of adsorption experiment on sample B1

Table 9: Result of adsorption experiment on sample B1 for day 2,3 and 10

Sample	Amount of GAC	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g)
B1-1	0.1944	50	0.009	0.1932	50	9.6581	254.7176	254.717
B1-2	0.1518	50	0.304	4.7152	75	353.6412	212.8982	212.898
B1-3	0.116	50	0.472	7.2905	50	364.5244	273.9119	273.911
B1-4	0.0839	50	0.555	8.5628	62.5	535.1747	277.0115	277.011
B1-5	0.0543	50	0.84	12.9316	62.5	808.2225	176.5907	176.590

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g)
B1-1	0.1944	48	0.003	0.101187	50	5.05935	1.135481	255.853
B1-2	0.1518	48	0.086	1.373494	75	103.0121	79.25032	292.148
B1-3	0.116	48	0.284	4.408636	50	220.4318	59.62452	333.536
B1-4	0.0839	48	0.148	2.323892	62.5	145.2433	223.0835	500.095
B1-5	0.0543	48	0.314	4.868506	62.5	304.2816	445.4726	622.063

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Dq (mg/g)	q (mg/g)
B1-1	0.1944	46	0.003	0.1012	50	5.0594	0.0000	255.853
B1-2	0.1518	46	0.112	1.7720	75	132.9036	-9.0580	283.090
B1-3	0.116	46	0.243	3.7801	50	189.0074	12.4614	345.997
B1-4	0.0839	46	0.147	2.3086	62.5	144.2852	0.5253	500.620
B1-5	0.0543	46	0.253	3.9334	62.5	245.8398	49.5087	671.572

7.4 APPENDIX 4: Result of adsorption experiment on sample B3

Table 10: Result of adsorption experiment on sample B3

Sample B3

Day 2

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Δq (mg/g)	q (mg/g)
B3-1	0.19	50	0.08	1.28	50	64.08	240.72	240.7
B3-2	0.15	50	0.22	3.38	75	253.62	245.84	245.8
B3-3	0.12	50	0.28	4.32	50	215.83	338	33
B3-4	0.08	50	0.43	6.57	62.5	410.63	351.24	351.2
B3-5	0.05	50	0.66	10.14	62.5	633.86	337.15	337.1

Day 3

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Δq (mg/g)	q (mg/g)
B3-1	0.19	48	0.01	0.16	50	8.13	13.82	254.5
B3-2	0.15	48	0.13	2.09	75	157.05	30.54	276.3
B3-3	0.12	48	0.2	3.14	50	156.82	24.42	362.4
B3-4	0.08	48	0.23	3.5	62.5	219.01	109.62	460.8
B3-5	0.05	48	0.44	6.82	62.5	425.96	183.78	520.9

Day 10

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Δq (mg/g)	q (mg/g)
B3-1	0.19	46	0	0.09	50	4.29	0.91	255.44
B3-2	0.15	46	0.13	2.08	75	155.9	7.32	283.7
B3-3	0.12	46	0.18	2.86	50	143.02	5.47	367.89
B3-4	0.08	46	0.22	3.38	62.5	211.35	4.2	465.06
B3-5	0.05	46	0.43	6.65	62.5	415.42	8.93	529.86

Day 12

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Δq (mg/g)	q (mg/g)
B3-1	0.19	44	-0.01	-0.11	50	-5.67	2.26	257.7
B3-2	0.15	44	0.13	2.02	75	151.3	1.33	278.06
B3-3	0.12	44	0.18	2.85	50	142.25	0.29	368.19
B3-4	0.08	44	0.21	3.29	62.5	205.6	3.01	468.08
B3-5	0.05	44	0.43	6.65	62.5	415.42	0	529.86

7.5 APPENDIX 5: Result of adsorption experiment on sample C3

Table 11: Result of adsorption experiment on sample C3

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Δq (mg/g)	c (mg
C3-1	0.19	50	0.01	0.16	50	8.13	255.11	255
C3-2	0.15	50	0.15	2.34	75	175.44	271.59	271
C3-3	0.12	50	0.24	3.66	50	182.88	352.21	352
C3-4	0.08	50	0.38	5.8	62.5	362.72	379.78	379
C3-5	0.05	50	0.49	7.57	62.5	472.9	485.36	485

Day 3

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Δq (mg/g)	q (mg
C3-1	0.19	48	0.01	0.19	50	9.66	-0.38	254
C3-2	0.15	48	0.06	0.93	75	69.67	33.45	305
C3-3	0.12	48	0.16	2.57	50	128.46	22.52	374
C3-4	0.08	48	0.15	2.37	62.5	148.12	122.78	502
C3-5	0.05	48	0.39	6	62.5	375.18	86.38	571

Day 10

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Δq (mg/g)	q (mg
C3-1	0.19	46	0.01	0.13	50	6.59	0.73	255
C3-2	0.15	46	0.05	0.84	75	62.77	2.09	307
C3-3	0.12	46	0.16	2.55	50	127.69	0.3	375
C3-4	0.08	46	0.15	2.29	62.5	143.33	2.63	505
C3-5	0.05	46	0.39	5.97	62.5	373.26	1.62	573

Day 12

Sample	Amount of AC (g)	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	Δq (mg/g)	q (mg
C3-1	0.19	44	0	-0.01	50	-0.31	1.56	257
C3-2	0.15	44	0.05	0.84	75	62.77	0	307
C3-3	0.12	44	0.14	2.19	50	109.3	6.98	382
C3-4	0.08	44	0.14	2.25	62.5	140.45	1.51	50
C3-5	0.05	44	0.38	5.91	62.5	369.43	3.11	576