Atrazine Removal by an Adsorbent Synthesized from Water Hyacinth

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การกำจัดอาทราซีนด้วยตัวดูดซับที่สังเคราะห์จากผักตบชวา

สิตานันท์ นันทมงคล

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By Ms. Sitanan Nuntamongkol
Field of Study Petrochemical Engineering
Advisor Dr. Patthranit Wongpromrat

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Abstract

Water hyacinth was used as a raw material to produce 3 different types of activated carbon, that were untreated activated carbon (AC), HCl-treated activated carbon (HCl-AC) and NaOH-treated activated carbon (NaOH-AC), in order to determine a suitable preparation method of activated carbon for atrazine removal from water. After pyrolysis, most of NaOH-AC became ash. Therefore, there were only 2 types of activated carbon (AC and HCl-AC) used in this work for comparing their surface areas and adsorption efficiencies. Comparing with untreated method, HCl treatment could improve the carbon content and surface area from 38.921% to 71.192% and 160.2 to 436.0 m^2/g, respectively. The adsorption capacities and adsorption efficiencies of AC and HCl-AC were compared by using them to remove 12 ppm of atrazine concentration. The results revealed that, among these adsorbents, HCl-AC was probably the best one for removing atrazine from water with the adsorption capacity and adsorption efficiency of 23.54 mg/g and 75.58%, respectively while AC could remove atrazine with the adsorption capacity and adsorption efficiency of 18.78 mg/g and 59.76%. Furthermore, the adsorption isotherm of HCl-AC was studied by varying atrazine concentrations in the range of 0-15 ppm. The results showed that its isotherm tended to fit Langmuir equation that means the adsorption of atrazine by HCl-AC was chemical adsorption. In addition, the kinetics of adsorption of HCl-AC was also determined by adsorbed 15 ppm of atrazine solution until the process reached its equilibrium. The results showed that its kinetics of adsorption tended to fit Psuedo-second-order kinetics model that means its adsorption phenomenon was limited by adsorption process (reaction limit) and it needs 2 active sites of adsorbent to adsorb one molecule of atrazine.

Keywords: Atrazine removal, Water hyacinth, Activated carbon

เรื่อง	การกำจัดอาทราซีนด้วยตัวดูดซับที่สังเคราะห์จากผักตบชวา
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บทคัดย่อ

งานวิจัยนี้มีจุดประสงค์เพื่อกำจัดอาทราซีนซึ่งเป็นสารฆ่าแมลงชนิดหนึ่งออกจากน้ำ โดยใช้ตัวดูดซับที่สังเคราะห์จากผักตบชวา โดยผักตบชวาจะถูกนำมาสังเคราะห์เป็นถ่านกัมมันต์ และกระตุ้นด้วยวิธีการต่างๆ 3 วิธี ซึ่งจะทำให้ได้ถ่านกัมมันต์ทั้งหมด 3 ชนิด ได้แก่ ถ่านกัมมันต์ที่ไม่ได้รับการกระตุ้น (AC) ถ่านกัมมันต์ที่ถูกกระตุ้นด้วยกรดไฮโดรคลอริก (HCl-AC) และถ่านกัมมันต์ที่ถูกกระตุ้นด้วยโซเดียมไฮดรอกไซด์ (NaOH-AC) หลังจากการเตรียมถ่านกัมมันต์พบว่า NaOH-AC ส่วนใหญ่เปลี่ยนเป็นเถ้าหลังจากผ่านการเผาที่อุณหภูมิ 500°C เป็นเวลา 1 ชั่วโมง ดังนั้นในวิจัยนี้จึงทำการเปรียบเทียบพื้นที่ผิวและความสามารถในการดูดซับของ AC และ HCl-AC เท่านั้น เมื่อเปรียบเทียบลักษณะของถ่านกัมมันต์ที่ไม่ถูกกระตุ้นกับถ่านกัมมันต์ที่ถูกกระตุ้นด้วยกรดไฮโดรคลอริก พบว่า การเตรียมถ่านกัมมันต์แบบกระตุ้นด้วยกรดไฮโดรคลอริกสามารถเพิ่มเปอร์เซ็นต์คาร์บอนจาก 38.921% เป็น 71.192% และเพิ่มพื้นที่ผิวของถ่านกัมมันต์ จาก 160.2 m^2/g เป็น 436.0 m^2/g และเมื่อเปรียบเทียบความสามารถในการดูดซับ โดยการนำถ่านกัมมันต์ทั้งสองชนิดมาดูดซับสารละลายอาทราซีนเข้มข้น 12 ppm พบว่า ความสามารถในการดูดซับของ HCl-AC มากกว่า AC โดยมีค่าเท่ากับ 23.54 mg/g และสามารถกำจัดอาทราซีนได้ถึง 75.58% ในขณะที่ความสามารถในการดูดซับของ AC มีค่าเท่ากับ 18.78 mg/g ซึ่งสามารถกำจัดอาทราซีนได้ 59.76% จากผลข้างต้นทำให้ทราบว่า HCl-AC น่าจะเป็นถ่านกัมมันต์ที่เหมาะสมที่สุดสำหรับการกำจัดอาทราซีนออกจากน้ำ และเมื่อศึกษาไอโซเทอมการดูดซับของ HCl-AC โดยการเปลี่ยนความเข้มข้นตั้งต้นของสารละลายอาทราซีนให้อยู่ในช่วง 0-15 ppm พบว่า ไอโซเทอมการดูดซับของ HCl-AC มีแนวโน้มสอดคล้องตามสมการแลงเมียร์ ซึ่งหมายความว่า การดูดซับอาทราซีนของ HCl-AC เป็นการดูดซับทางเคมี นอกจากนี้งานวิจัยนี้ยังได้ศึกษาจลนพลศาสตร์การดูดซับของ HCl-AC อีกด้วย โดยให้ถ่านกัมมันต์ดูดซับสารละลายอาทราซีนเข้มข้น 15 ppm จนกระทั่งระบบเข้าสู่สมดุล ซึ่งพบว่า จลนพลศาสตร์การดูดซับของ HCl-AC มีแนวโน้มสอดคล้องกับ โมเดล Pseudo-second-order ซึ่งหมายความว่า การดูดซับอาทราซีนของ HCl-AC ถูกจำกัดด้วยขั้นตอนการดูดซับอาทราซีนบนตัวดูดซับ และต้องใช้ตำแหน่งกัมมันต์ (active site) จำนวน 2 ตำแหน่งในการดูดซับอาทราซีนหนึ่งโมเลกุล

คำสำคัญ: การกำจัดอาทราซีน, ผักตบชวา, ถ่านกัมมันต์

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Sitanan Nuntamongkol

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NOMENCLATURE

A_T	Temkin isotherm equilibrium binding constant (L/g).
B	Constant related to heat of adsorption.
b_T	Temkin isotherm constant (J/mol).
C	Intraparticle diffusion constant (mg/g).
C_0	Initial concentration of solution (mg/L).
C_e	Equilibrium concentration of adsorbate remains in solution (mg/L).
K_F	Freundlich isotherm constants (mg/g).
K_L	Langmuir isotherm constant related to Energy of adsorption (L/mg).
k_1	Pseudo-first-order equilibrium rate constant (1/min).
k_2	Pseudo-second-order equilibrium rate constant (g/ mg min).
k_p	Rate constant for intraparticle diffusion (mg/g min$^{1/2}$).
M	Weight of an adsorbent (g).
n	Adsorption intensity.
q_e	Equilibrium concentration of adsorbate on surface of adsorbent or adsorption capacity (mg/g).
q_m	Maximum adsorption capacity (mg/g).
q_t	Amount of adsorbed adsorbate (mg/g).
R	Gas constant (8.314 J/mol K).
R_L	Equilibrium parameter or separation factor.
RSD	Relative standard deviation.
r	Radius of particle of adsorbent (cm).
T	Absolute temperature (K).
t	Time (min).
V	Volume of solution (L).

CHAPTER I
INTRODUCTION

1.1 Background

Thailand is an agricultural country where exports various kinds of agricultural products. Therefore, there is the using of some chemicals for producing high-quantity agricultural products. Herbicide is one kind of chemicals which is widely used to control weeds. Thailand imports the large amount with high value of herbicide between 2010-2015 [1]. Atrazine is the Thailand top ten imported organochloride herbicide [2]. It is used to control weeds in farms and crop land sand for example corn, sugarcane, or millet farm. Due to its extensive usage, atrazine can contaminate in soil and water resources and it has half-life in that resources about 13-261 days and more than 200 days, respectively [3]. This affects the contamination in surface water and ground water of Thailand [4]. Atrazine also affects to frog mutation [5], ecology [4] and human health [6]. Therefore, because of its hazard, it is necessary to remove atrazine from water resources.

The atrazine removal techniques from water are incineration, reverse osmosis, electrodialysis, chemical degradation and etc. Nevertheless, all of these techniques are costly and produce corrosive and toxic gases [7]. Adsorption is a simply attractive method since the atrazine will be adsorbed on the adsorbent's surface. One of the common adsorbent is an activated carbon because of its high surface area and porosity. However, activated carbon is an expensive material thus it is necessary to develop a low cost effective carbon that can be used to remove the contaminant from water. One property affecting the adsorption capacity is porosity which depends on nature of raw material and activation method. Due to the large amount of agricultural wastes existing in Thailand, there are many studies using these agricultural wastes, for example coconut shell, watermelon peel, rice straw and etc., to produce an effective activated carbon. Meanwhile, Thailand has faced a problem of water hyacinth. A water hyacinth (*Eichhornia crassipes*) is a free-floating perennial aquatic plant which can propagate and grow easily. The large amount of water hyacinth makes rotten water because oxygen cannot dissolve into water, blocks waterways, affects both navigation and drainage, and increases siltation and flooding probabilities.

In the consequence, this study aims to prepare a low cost activated carbon from water hyacinth for atrazine adsorption. This means that this study changes waste material (water hyacinth) to be a valuable material. As complex structure of atrazine, chemical and physical treatments are needed to increase the porosity of water hyacinth. The effect of different kinds of activated carbon preparation methods on adsorption efficiency was investigated. The equilibrium and kinetics of adsorption were also determined in this work.

1.2 Objectives

1. To determine a suitable preparation method of activated carbon for atrazine removal from water.
2. To study the effect of different kinds of activated carbon preparation methods on adsorption efficiency.
3. To determine the suitable kinetics model and adsorption isotherm of the best activated carbon prepared in this work for atrazine adsorption.

1.3 Scopes of Work

1. Preparation methods of adsorbent
    1.1 Untreated activated carbon (AC)
    1.2 Treated activated carbon by HCl (HCl-AC)
    1.3 Treated activated carbon by NaOH (NaOH-AC)

2. Adsorption experiments
    2.1 Comparison of the adsorption efficiencies of different kinds of activated carbon preparation methods.
    2.2 Equilibrium study: to identify the adsorption isotherm.
    2.3 Kinetics study: to identify the kinetics model of adsorption.

2.4 Expected Outputs

1. The suitable preparation method of activated carbon from water hyacinth for atrazine removal is attained.
2. The kinetics model and adsorption isotherm which can describe an adsorption phenomenon of adsorbent are specified.

CHAPTER II
THEORY AND LITERATURE REVIEW

2.1 Atrazine [8]

Atrazine ($C_8H_{14}ClN_5$) is an organochloride herbicide used to control weeds in farms and crop land sand.

- Chemical name: 2-Chloro-4-ethylamino-6-isoproplyamino-s-triazine
- Trade name: 6-Chloro-N-ethyl-N'-isopropyl-1,3,5-triazine-2,4-diamine
- Its chemical structure is shown in Figure 2.1

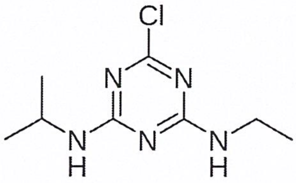

Figure 2.1 Chemical structure of atrazine [8].

- Molecular weight: 215.685 g/mol
- Molecular size: 10.36 Å [29]
- Chemical and physical properties of the pure substance
  - Appearance: Colorless, crystalline solid
  - Odor: Odorless
  - Melting-point: 173-175°C
  - Density: 1.187 g/cm^3 at 20°C
  - Solubility:
    - Slightly soluble in water (33 mg/L at 25°C)
    - Soluble in acetone, chloroform, dichloromethane, ether, ethyl acetate, n-hexane, methanol, n-octanol and toluene
  - Vapor pressure: 0.04 mPa at 20°C

2.2 Water Hyacinth

Water Hyacinth (*Eichhornia crassipes*) is a free floating perennial aquatic plant with dark green thick leaves and purple flowers as showed in Figure 2.2. It is found on the surface of the rivers, lakes, canals and ponds. A water hyacinth can propagate rapidly by stolons, buds, and other asexual parts, as well as by seeds. The water hyacinth stem has a sponge-like structure therefore it has high ability to adsorb moisture from air and water [9, 10].

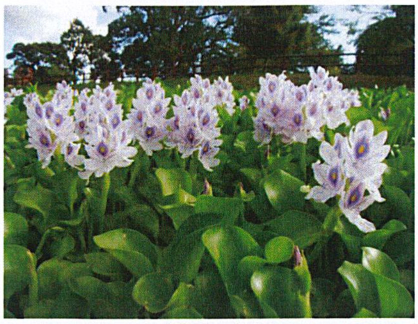

Figure 2.2 Water hyacinth [11].

Water hyacinth consists of many compositions which is shown in Table 2.1.

Table 2.1 Composition in dried water hyacinth [12].

Composition	**Percent**
Lignin	12-13
Cellulose	43-44
Pentosane	14-15
Nitrogen	2.8-3.5
Sodium	1.5-2.5
Potassium	2.0-3.5
Calcium	0.6-1.3

Because water hyacinth can propagate easily, therefore it causes a prolong problem in water resources of Thailand. There are 3 common restriction methods for water hyacinth [12].

1. Chemical restriction: Using of various types of chemicals, for example dalapon, diquat and paraquat, to restrict water hyacinth. This method has high efficiency to decrease the water hyacinth population but chemicals can affect the environment and aquatic animals.

2. Mechanical restriction: Using a labor or machine to restrict the water hyacinth but the long period of time is required and it is practical for only small size of water resources.

3. Biological restriction: Using bacteria, fungi, virus or insects to restrict water hyacinth.

2.3 Activated carbon [27, 28]

An activated carbon is a form of carbon that is treated to create a high porous structure between carbon atoms. Due to its high surface area, activated carbon is used as an adsorbent for contaminant removal by trapping the in their small pores. The characteristics of carbon materials, for example particle size, pore size, surface area and surface chemistry, affect the adsorption efficiency. Generally, the properties of raw material that can be made as the activated carbon are as follow.

1. Low volatile substance
2. High carbon molecule as a major component
3. Cheap, low valuable, or waste

The activated carbons are commonly prepared by two steps.

1. Carbonization: It is a method that pyrolyses the substance in furnace at high temperature about 200-500 °C with the absence of oxygen for avoiding a completed combustion of material. It helps to reduce the non-carbon substance by breaking the molecule and let them vaporize. The raw material will be changed into a block solid form called charcoal.

2. Activation: It is a method that is used to increase surface area and pore volume of substance. It consists of 2 methods:

1. Physical activation: Using high temperature to heat the substance with the presence of gas for example steam, CO_2, and etc. It is an environmental friendly method but a long period of time is required.

2. Chemical activation: Using the chemical as an activator, the reaction occurs and eliminates other molecules in precursor's pores. This method requires shorter period of time than that of physical activation, lower temperature and can increase the porosity more than physical activation method. The common chemicals used for activation are H_3PO_4, KOH, K_2CO_3, and $ZnCl_2$.

2.4 Adsorption [13]

Adsorption is a phenomenon of molecules of gas, liquid, or dissolved solids adhered or stuck onto the surface of solid. The solid substance used for adsorption is called adsorbent, on the other hand, the substance in the fluid stream that is adsorbed on the adsorbent is called adsorbate.

2.4.1 Adsorption mechanism [14]

There are 3 steps in adsorption:

1. Adsorbate diffuses to adsorbent surface.
2. Adsorbate migrates into pores of adsorbent.
3. Adsorbate monolayer buildup.

2.4.2 Types of adsorption [15, 16]

Based on nature of forces existing between adsorbent and adsorbate, adsorption can be separated into 2 types that are

1. Physical adsorption

Physical adsorption or physisorption occurs when the force of attraction between adsorbent and adsorbate is very weak force or Vander Waal's force. Therefore, physisorption can be reversed or desorbed when the temperature is elevated or pressure is decreased. This type of adsorption is not very specific and can form multilayer of adsorption as shown in Figure 2.3.

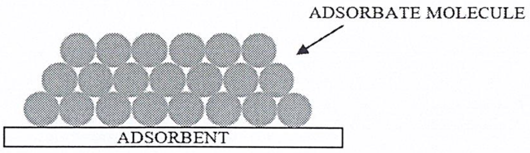

Figure 2.3 Physical Adsorption [17].

2. Chemical adsorption

Chemical adsorption or chemisorption occurs when the force of attraction between adsorbent and adsorbate is strong force or almost the same strength as chemical bond. Therefore, chemisorption is difficult to reverse or desorb. It is highly specific and forms monolayer of adsorption as show in Figure 2.4.

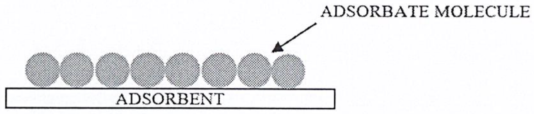

Figure 2.4 Chemical Adsorption [17].

2.4.3 Factors affecting adsorption [18, 19]

1. The surface area of adsorbent: The adsorption capacity depends on surface area of adsorbent. The higher surface area can increase adsorption capacity. With the same amount of adsorbent, the finer adsorbent gives higher surface area.
2. Nature of adsorbate: An adsorption efficiency increases with decreasing solubility of solvent due to the low interaction force between solute and solvent.
3. Temperature of solution: As the adsorption is exothermic process therefore high solution temperature decreases an adsorption efficiency.
4. Contact time: The longer contact time can increase an adsorption efficiency.

2.4.4 Adsorption equilibrium

If the adsorbent and adsorbate are contacted long enough, an equilibrium between the amount of adsorbate adsorbed and the amount of adsorbate in solution will be reached. The equilibrium relationship is described by an adsorption isotherm.

Adsorption isotherm [20-26, 31]

Adsorption isotherm is a curve that can determine the adsorption capacity of an adsorbent. It shows the relationship between equilibrium concentration of adsorbate on surface of adsorbent or adsorption capacity (q_e) in the unit of milligram of adsorbate per gram of adsorbent (mg/ g) and equilibrium concentration of adsorbate remaining in solution (C_e) in the unit of milligram of solute per liter of solution (mg/L) at constant temperature.

The adsorption capacity of adsorbent can be calculated from Equation 2.1

$$q_e = \frac{(C_0 - C_e) \times V}{M} \tag{2.1}$$

where C_0, V and M represent the initial concentration of solution (mg/L), volume of solution (L) and weight of an adsorbent (g), respectively. The adsorption efficiency can be calculated from Equation 2.2.

$$efficiency, \% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2.2)$$

The relationship of adsorption capacity and equilibrium concentration of adsorbate remaining in solution depends on the type of adsorption that is chemical adsorption or physical adsorption. There are 3 common isotherm models concerned in this work:

1. Langmuir isotherm:

It depends on the assumption that the monolayer adsorption occurs on the homogenous surface with a specific number of sites, therefore, there are no further adsorption can take place at occupied site.

Langmuir's equation is shown in Equation 2.3.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2.3)$$

Its linearized form is shown in Equation 2.4.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (2.4)$$

When the relationship between C_e and $\frac{C_e}{q_e}$ is plotted as shown in Figure 2.5, K_L is Langmuir isotherm constant in the unit of L/mg which related to energy of adsorption and q_m is the maximum adsorption capacity in the unit of milligram of adsorbate per gram of adsorbent (mg/g) are obtained from the intercept of y-axis and the slope of the graph, respectively.

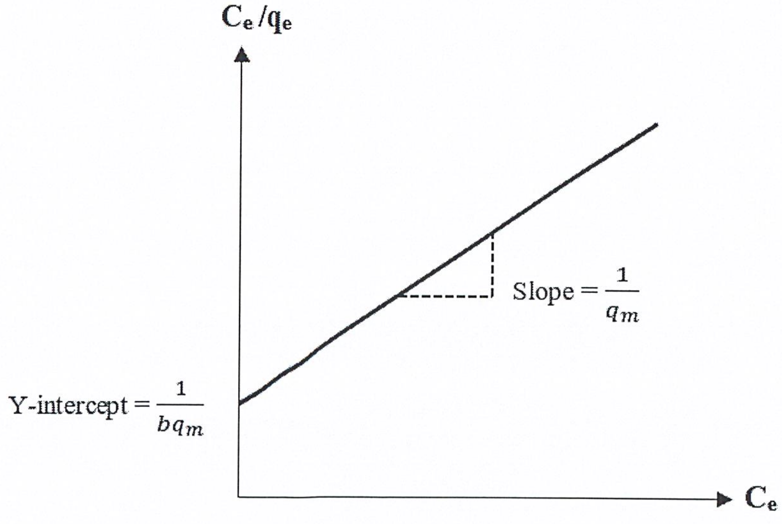

Figure 2.5 The plot of Langmuir adsorption isotherm.

The essential characteristics of Langmuir isotherm can also be expressed in terms of dimensionless constant R_L which represents an equilibrium parameter or separation factor as shown in Equation 2.5.

$$R_L = \frac{1}{1 + K_L C_0} \tag{2.5}$$

The R_L value indicates the adsorption nature to be either favorable if $0 < R_L < 1$, linear if $R_L = 1$, unfavorable if $R_L > 1$ or irreversible if $R_L = 0$.

2. Freundlich isotherm:

It is an empirical equation used to describe the multilayer adsorption on the heterogeneous surface of an adsorbent.

Freundlich's equation is shown in Equation 2.6.

$$q_e = K_F C_e^{\frac{1}{n}} \quad . \tag{2.6}$$

Its linearized form is shown in Equation 2.7.

$$log q_e = \frac{1}{n} log C_e + log K_F \quad . \tag{2.7}$$

When $logC_e$ and $logq_e$ are plotted as shown in Figure 2.6, K_F and $1/n$ that are Freundlich constants representing adsorption capacity in the form of multilayer adsorption (mg/g) and adsorption intensity, respectively, are obtained from the slope and intercept of a graph respectively.

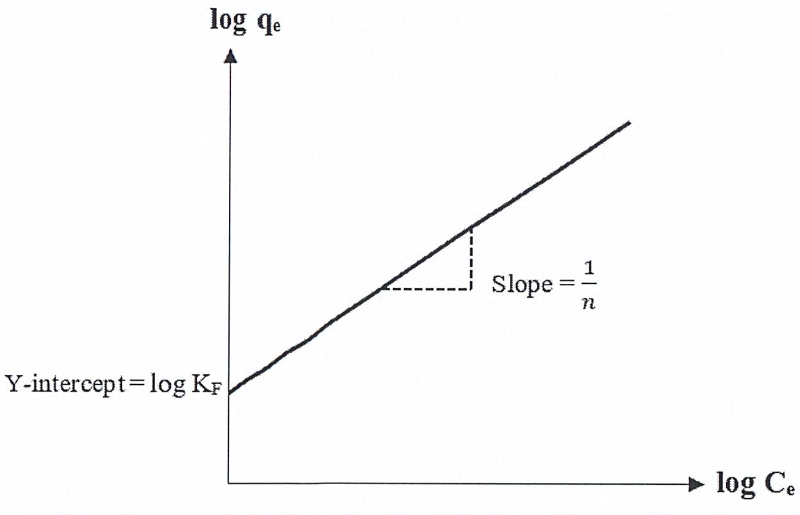

Figure 2.6 The plot of Freundlich adsorption isotherm.

3. Temkin isotherm:

This type of isotherm is used to describe the chemical adsorption because it contains factor taking into account of adsorbent and adsorbate interactions. With an ignorance of the extremely low and large value concentrations, it has assumption that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic. The model is given in Equation 2.8.

$$q_e = \frac{RT}{b_T} ln(A_T C_e) \tag{2.8}$$

The linearized form is shown in Equation 2.9.

$$q_e = \frac{RT}{b_T} lnA_T + \left(\frac{RT}{b_T}\right) lnC_e \tag{2.9}$$

B is used to substitute$\frac{RT}{b_T}$, therefore, the model can be written as in Equation 2.10.

$$q_e = BlnA_T + BlnC_e \tag{2.10}$$

where A_T= Temkin isotherm equilibrium binding constant (L/g)
b_T= Temkin isotherm constant (J/mol)
R= gas constant (8.314 J/mol/K)
T= Absolute temperature (K)
B= Constant related to heat of adsorption

2.4.5 Adsorption kinetics models [20, 23-24, 26, 32-34, 36]

Adsorption kinetics model is used to evaluate the adsorption rate. There are many kinetics models for example Boyd, Weber and Morris, Pseudo-first-order, and Pseudo-second-order.

1. Boyd model

This kinetics model reveals that the mass transfer into the interior of particle or intraparticle diffusion is the slowest step. It is generally used with long duration time or $\frac{q_t}{q_e}$ is more than 0.85. This kinetics model describing the homogenous diffusion of adsorbate in sphere adsorbent and assuming a constant surface diffusivity D_s (cm^2/min) at all points in particle is shown in Equation 2.11.

$$\frac{\partial q_t}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial q_t}{\partial r}) \tag{2.11}$$

which q_t is amount of adsorbed adsorbate (mg/g) and r is radius of particle of adsorbent (cm). The Boyd equation is shown in Equation 2.12.

$$\frac{q_t}{q_e} = 1 - (\frac{6}{\pi^2})exp(\frac{-D_s\pi^2 t}{r^2}) \tag{2.12}$$

Its linearized form is shown in Equation 2.13.

$$ln\left(1 - \frac{q_t}{q_e}\right) = ln\left(\frac{6}{\pi^2}\right) - (\frac{D_s\pi^2 t}{r^2}) \tag{2.13}$$

2. Weber and Morris model

It describes that intraparticle diffusion is the slowest step. Weber and Morris studied the batch adsorption. The equation of Weber and Morris model is shown in Equation 2.14.

$$q_t = k_p t^{\frac{1}{2}} + C \tag{2.14}$$

where q_t is the amount of adsorbed adsorbate (mg/g), k_p is rate constant for intraparticle diffusion (mg/ g min$^{1/2}$) which can be obtained from slope of the graph and C is intraparticle diffusion constant (mg/g) which is direct proportional to the boundary thickness can be obtained from Y-intercept value of the graph. A larger C suggests a greater boundary layer effect.

3. Pseudo-first-order

This model describes that adsorption is the slowest step. In Equation 2.15 shows that there is using one adsorbent active site to adsorb one molecule of adsorbate.

$$A + S \leftrightarrow A * S \tag{2.15}$$

where A represents adsorbate, S represents adsorbent and $A*S$ represents adsorbed compound. It has 5 assumptions there are:

1. Adsorption only occurs on localized sites and involves no interaction between the adsorbed ions.
2. The adsorption energy is not dependent on surface coverage.
3. The maximum adsorption corresponds to a saturated monolayer of adsorbates on adsorbent surface.
4. The concentration of adsorbate is considered to be constant.
5. The adsorbed ion on adsorbent is governed by a first-order rate equation.

The pseudo-first-order equation can be written as Equation 2.16

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.16}$$

k_1 is pseudo-first-order equilibrium rate constant in the unit of 1/min, q_t is amount of adsorbed solute at any time in unit of mg/g and q_e is the amount of adsorbed solute at equilibrium in unit of mg/g.

An integrating form is shown in Equation 2.17.

$$log \frac{q_e}{q_e - q_t} = \frac{k_1}{2.303} t \tag{2.17}$$

And the linearized form as shown in Equation 2.18

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} t \tag{2.18}$$

The values of k_1 is obtained from a slope of a plot between $\log(q_e - q_t)$ and t.

4. Pseudo-second-order:

The kinetics of adsorbent removal are described by Equation 2.19. It described that two adsorbent active sites are required to adsorb one molecule of adsorbent. The assumptions of pseudo-second-order model are almost the same as pseudo-first-order model except the adsorbed ion on adsorbent is governed by a second-order rate equation.

$$A + 2S \leftrightarrow A * S_2 \qquad (2.19)$$

The pseudo-second-order is written Equation 2.20.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (2.20)$$

where k_2 represents pseudo- second- order equilibrium rate constant in unit of g /mg min.

An integrating form is in Equation 2.21.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} - k_2 t \qquad (2.21)$$

A linearized form is shown in Equation 2.22.

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \qquad (2.22)$$

The value of k_2 (g /kg min) is obtained from the intercept of a plot between $\frac{t}{q_t}$ and t.

2.5 Literature Review

Gupta V.K. et al. [19] studied a methoxychlor, atrazine and methyl parathion removal from waste water by activated carbon prepared from waste rubber tire. The activated carbon prepared from thermal and chemical treatments of waste rubber tire. The chemical treatment using KOH can activate the adsorbent by developing porosity of adsorbent and incorporating carbonyl and hydroxyl functional groups on adsorbent surface. The temperature of thermal treatment was at 900°C for 2 hours. The best condition for removing pesticide from waste water was the use of 200- 250 μm of adsorbent, 60 minutes contact time with low pH and low temperature of pesticide waste water. Gas Chromatography (GC) method was chosen for determining pesticide concentration. A 1 μL of sample was injected into HP-5 with silica capillary column and 1.0 mL/min of helium carrier gas. The adsorbent had the adsorption capacities of 112.0 mg/g, 104.9 mg/g and 88.9 mg/g for removing 12 mg/L of methoxychlor, atrazine and methyl parathion (the removal efficiency are 93.3%, 87.4% and 74.1%), respectively. The results were confirmed by column experiment that can remove 91%, 82.1% and 71.78% of methoxychlor, atrazine and methyl parathion, respectively. The adsorption equilibrium obeyed Langmuir model and the kinetics data was well-described by pseudo-first-order model. This developed adsorbent is inexpensive and has high efficiency to remove pesticide from waste water.

Brahima S. et al. [20] studied an adsorption of heptachlor which is an organochloride pesticide by using activated carbon produced from wheat straw. The wheat straw activated carbon was treated by H_3PO_4 and then be heated at 500 °C. The effects of pH, activated carbon concentration and heptachlor concentration on adsorption efficiency were investigated. The results showed that under neutral and acidic conditions, the adsorption efficiency was increased above 97% but in basic conditions the adsorption efficiency was 84%. Also, the heptachlor adsorption efficiency was increased from 92% to 97% when the activated carbon concentration was increased. In addition, there was no effect of higher concentration of heptachlor on adsorption efficiency. The maximum adsorption capacity of activated carbon was 2.218 mg/g. An experimental data was fitted to Langmuir isotherm equation and adsorption kinetics was also well-described by pseudo-second-order model.

Guangcai T. et al. [21] studied the atrazine removal from aqueous solution by using corn straw as a precursor for Na_2S-biochar, KOH-biochar and activated carbon. An activated carbon has the highest surface area with the value of 466.37 m^2/g while the surface area of Na_2S- and KOH-biochar were only 55.58 and 59.23, respectively. The adsorption efficiency was increased with decreasing solution pH. When compare the treated adsorbent with untreated one, the adsorption capacities of all adsorbents were increased by 38.66%, 46.39% and 47%, respectively. An equilibrium equation which was well-described all data from Na_2S-biochar, KOH-biochar and activated carbon was Langmuir isotherm equation and the kinetics models fitting to Na_2S-biochar, KOH-biochar and activated carbon were pseudo-first-order, pseudo-second-order and pseudo-second-order, respectively.

Abhishek M. et al. [22] studied the removal of atrazine and imidacloprid from water by using rice straw as an adsorbent. The rice straw adsorbents were separated into two types: a dried rice straw adsorbent and modified rice straw adsorbent. Rice straw was dried and pyrolysed in the furnace at 600°C for 1 hour. Then, it was grounded and sieved to be 150 μm diameter size. For modified adsorbent, a dried rice straw was soaked in 1M H_3PO_4 at 80°C for 1 hour, then, it was cooled down to room temperature and left overnight. After that, it was separated from solution by filtration and washed by distilled water until the pH of washed water became neutral. This adsorbent was soaked in 1000 mL of 0.05 M phosphate-citrate buffer for 2 hours for acidic removal. Lastly, it was dried at 80°C for 24 hours. The surface areas of untreated and treated adsorbents were 220.2 and 192.3 m^2/g, respectively. These adsorbents were used to remove 10 mg/L of atrazine and imidacloprid. The required dosage of both adsorbents to remove 75, 80, 85, 90 and 95% of atrazine from 1000 L solution were similar, therefore, both adsorbents had high efficiencies in adsorption. Their equilibrium data fitted to Freundlich equation.

El-Walil AM et al. [23] studied the removal of lead (Pb) from aqueous solution by adsorption using activated carbon and modified activated carbon prepared from dried water hyacinth plant. Activated carbon was treated by H_3PO_4 for 2 days at room temperature and then be heated at 550-600°C for 3 hours. For modified activated carbon, an activated carbon was treated by nitric acid (HNO_3)

again for increasing the formation of functional groups such as carboxylic acid. The results showed that activated carbon has the highest surface area with the value of 493.78 m^2/g. The increasing of Pb initial concentration resulted in the increasing of adsorption capacity. The optimum contact time was 60 minutes and the pH of solution was 5. An adsorption was also increased with increasing the dosage of adsorbent. The kinetics of adsorption fitted to pseudo- second- order and the equilibrium was well-described by Langmuir isotherm model.

Tina. O. I. et al. [24] studied the adsorption of 2-Nitrophenol by water hyacinth activated carbon. The water hyacinth stem was chopped into pieces, dried for 5-7 days and grounded in hammer mill. Then, it was impregnated with saturated solution of ammonium chloride (NH_4Cl), dried and heated at 400°C for 60 minutes. The activated carbon was washed by distilled water until the pH of washed water was neutral, dried at 102-105°C and grounded into powder. In this experiment, the effects of contact time, adsorbent dosage and initial concentration on adsorption efficiency were investigated. Only initial concentration of 2-Nitrophenol solution between 20-160 ppm affected adsorption. The experimental data was fitted to Langmuir isotherm with the capacity of 47.62 mg/g and pseudo-second-order kinetics model.

CHAPTER III

RESEARCH METHODOLOGY

This work aims to study the suitable adsorbent preparation method for atrazine removal by chemically and physically treated dried water hyacinth. The HCl and NaOH are chosen for chemical treatment in order to develop its surface area of the adsorbent. Then, surface area and pore diameter of all three types (untreated, HCl-treated and NaOH-treated) adsorbent are compared by using Brunauer-Emmett-Teller method (BET) and CHNS analysis is used for determining compositions of the adsorbents. The effect of different adsorbent preparation methods on adsorption efficiency is investigated. The best adsorbent is then chosen to identify its isotherm and kinetics model.

3.1 Materials and Chemicals

3.1.1 Materials

1. Knife
2. Scissors
3. Metal plate
4. 50 mL-Beaker
5. 250 mL-Beaker
6. 1000 mL-Beaker
7. 50 mL-Erlenmeyer flask
8. 1000 mL-Erlenmeyer flask
9. 1 mL-Pipette
10. 100 mL-Pipette
11. Pipette pump
12. Spatula
13. Test tube
14. Watch glass
15. Stirring rod
16. Glass funnel
17. Glass Jar
18. Magnetic bar
19. Magnetic stirrer plate
20. Plastic box
21. Sampling bottle
22. GC vial
23. Whatman Filter paper No.1
24. Oven
25. pH-meter
26. Furnace
27. Sieve shaker
28. Rotary shaker
29. Gas Chromatography

3.1.2 Chemicals

1. Water hyacinth
2. Hydrochloric acid
3. Sodium Hydroxide
4. Atrazine standard (Analytical grade)
5. Atrazine 90% W
6. Distilled water
7. n-Hexane

3.2 Activated carbon preparation

3.2.1 Dried water hyacinth preparation

1. Collect water hyacinth from river.
2. Remove stem, peel and clean with water.
3. Chop the stem into pieces with the thickness of 0.2 cm. and dry it under the sunlight for 3 days.
4. Put on metal tray and dry it at 105°C for water removal until its weight is constant.
5. Cool it down to room temperature.
6. Store them in plastic box.

3.2.2 Untreated adsorbent preparation

1. Pyrolyse the dried water hyacinth in the furnace where the samples are heated gradually under nitrogen at 500°C and then maintained at this temperature for 1 hour.
2. After cooling to room temperature, grind and sieve activated carbon by grinder and sieve shaker to be 150-250 mesh-size.
3. Store the activated carbon in glass jar.
4. Determined the untreated activated carbon characteristics by BET and CHNS Analysis.

*** * Note: Before using, dry activated carbon in oven at 90°C for moisture removal.**

3.2.3 HCl-treated adsorbent preparation

1. Prepare 1 L of 1 M HCl in 1000 mL-beaker.
2. Add 10 g of dried water hyacinth into solution.
3. Leave it for 2 days.
4. After 2 days, separate water hyacinth by filtration.
5. Clean the water hyacinth by distilled water until the pH of solution is neutral measured by pH-meter.
6. Put it on a metal tray and dry it at 105 °C for 1 days.
7. Pyrolyse the water hyacinth in furnace where the samples are heated gradually under nitrogen at 500°C and then maintained at this temperature for 1 hour.
8. After cooling to room temperature, grind and sieve activated carbon by grinder and sieve shaker to be 150-250 mesh-size.

9. Store the activated carbon in glass jar.
10. Determined the HCl-treated activated carbon characteristics by BET and CHNS Analysis.

** **Note: Before using, bake the activated carbon in oven at 90°C for moisture removal.**

3.2.4 NaOH-treated adsorbent preparation

Repeat all steps as HCl-treated adsorbent preparation but change the chemical from HCl to NaOH.

3.3 Atrazine solution preparation

3.3.1 Atrazine standard solution

3.3.1.1 Preparation of 20 ppm of atrazine standard stock solution

1. Prepare 50 mL of distilled water in 100mL-beaker.
2. Put 0.001 g. of atrazine standard (analytical grade) into beaker.
3. Heat the solution at 60 °C on hot-magnetic stirrer plate with 150 rpm for 24 hours (make sure all atrazine powder were dissolved).
4. After atrazine powder was dissolved, store the 20 ppm atrazine solution in amber bottle.

3.3.1.2 Preparation of 3, 6, 9, 12, and 15 ppm of atrazine standard solution

1. Pipette 1.5, 3, 4.5, 6, and 7.5 mL of stock solution for preparing 3, 6, 9, 12, and 15 ppm solution respectively.
2. Release them in 10mL-volumetric flasks separately.
3. Adjust the volume by distilled water.
4. Store all solution in amber bottles.

3.3.2 Atrazine solution for adsorption experiments

3.3.2.1 Preparation of 20 ppm of atrazine stock solution for adsorption experiments.

1. Weight 0.022 g. of atrazine 90%W and dissolve in distilled water.
2. Pour the solution in 1000mL-volumetric flask.
3. Adjust the volume by distilled water.
4. Store the solution in amber bottle.

3.3.2.2 Preparation of 3, 6, 9, 12, and 15 ppm of atrazine solution

1. Use 30, 60, 90, 120 and 150 mL of stock solution for preparing 3, 6, 9, 12, and 15 ppm solution respectively.
2. Pour the solution in 200mL-volumetric flak separately.
3. Adjust the volume by distilled water.
4. Pour each solution in 250mL-beaker for adsorption experiment.

3.4 Standard curve preparation

3.4.1 GC analysis condition

1. GC-MS was used
2. GC column: HP-5 (30 m × 0.25 mm I.D.).
3. Using helium as a carrier gas at the flow rate of 1.0 mL/min with 25 mL/min.
4. The temperature of the column was 260 °C.
5. The temperature of the injector was 230 °C.
6. The temperature of the detector was 310 °C.
7. The column temperature was programed with the initial temperature at 100 °C and held for 3 minutes, then it was ramped with the rate of 10 °C /min to 280 °C and held for 5 minutes.
8. The ion source temperature was 230 °C.
9. Full-scan acquisition mode was used in the range of 35-500.
10. Sample with the volume of 1 μL was injected into the GC.

3.4.2 GC Condition testing (Standard curve preparation by using atrazine in n-hexane)

1. Prepared 3, 6, 9, 12, 15, and 20 ppm of atrazine (analytical grade) in n-hexane.
2. Pipetted 1.5 mL of each solution into GC vials.
3. Injected atrazine solution into GC.
4. Plotted standard curve with the relation of concentration (x-axis) and the area under atrazine curve obtained from GC detection (y-axis). The regression of the plot (R^2) was then reported.
5. Validated the method of analysis and the calibration curve by injecting 5 and 14 ppm of atrazine solution into GC and interpreting the area under the curve into atrazine concentration. The value of relative standard deviation (RSD) of validation should less than 10 and for % recovery value should between 60-120%. The details of validation method is explained in **Appendix B**.

3.4.3 Standard curve preparation

1. Prepared 3ppm of atrazine (analytical grade) in distilled water.
2. Pipetted 1 mL of solution into 50 mL-Erlenmeyer flask and added 2 mL of n-hexane to the flask.
3. Put in rotary shaker with 150 rpm for 10 minutes.
4. After 10 minutes, poured the solution into the test tube and left it until solution separated into 2 layers.
5. Pipetted 1.5 mL of upper layer of solution into GC vials.
6. Injected the sample into GC.
7. Plotted standard curve with the relation of concentration (x-axis) and the area under atrazine curve obtained from GC detection (y-axis). The regression of the plot (R^2) was then reported.

8. Repeated all steps with the atrazine concentrations of 6, 9, 12, 15 and 20 ppm.

3.5 Adsorption experiment

3.5.1 Study the effect of activated carbon preparation methods on adsorption

1. Prepared 200 mL of 12 ppm of atrazine into 250 mL-beaker.
2. Put the beaker on magnetic stirrer plate and put magnetic bar in the beaker.
3. Started the machine with the stirring rate of 150 rpm.
4. Added 0.1 g of activated carbon into beaker.
5. Pipetted 1 mL of samples at 60, 120, 180, 240, 300, and 1440 minutes by using 1 mL-pipette.
6. Released sample into sampling bottle through filter paper for adsorbent removal.
7. Pipetted 1 mL of each sample and 2 mL of n-hexane into 50 mL-Erlenmeyer flask.
8. Put them in rotary shaker with 150 rpm for 10 minutes.
9. After 10 minutes, poured all solutions into each test tube.
10. Left them until the solution separated into two layers.
11. Pipetted 1.5 mL of upper layer of solution into GC vial.
12. Analyzed concentration of samples by Gas Chromatography.

** **Note: Repeated all steps by changing the type of activated carbon.**

Only the most efficient adsorbent was used to study the adsorption kinetics and isotherm as the procedures in the sections 3.4.2 and 3.4.3.

3.5.2 Isotherm study experiment

1. Prepare 200 mL of 3 ppm of atrazine into 250mL-beaker.
2. Put the beaker on magnetic stirrer plate and put magnetic bar into beaker.
3. Start the machine with stirring rate of 150 rpm.
4. Added 0.1 g of activated carbon into beaker.
5. Left it for 120 minutes.
6. Pipetted 1 mL of sample by using 1 mL pipette.
7. Released sample into sampling bottle pass through filter paper for adsorbent removal.
8. Pipetted 1 mL of each sample and 2 mL of n-hexane into 50 mL-Erlenmeyer flask.
9. Put them in rotary shaker with 150 rpm for 10 minutes.
10. After 10 minutes, pour all solutions into each test tube.
11. Left them until the solution separates into two layers.
12. Pipetted 1.5 mL of upper layer of solution into GC vial.
13. Analyzed concentration of sample by Gas Chromatography.

** **Note: Change the atrazine initial concentration to 6, 9, 12, and 15 ppm then repeat all steps as mentioned above.**

3.5.3 Kinetics study experiment

1. Prepared 200 mL of 15 ppm of atrazine into 250 mL-beaker.
2. Put the beaker on magnetic stirrer plate and put magnetic bar in the beaker.
3. Start the machine with stirring rate of 150 rpm.
4. Added 0.1 g of activated carbon into beaker.
5. Pipetted 1 mL of sample by using 1 mL-volumetric pipette at 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 180, 240, 300, and 1440 minutes.
6. Released sample into sampling bottle pass through filter paper for adsorbent removal.
7. Pipetted 1 mL of each sample and 2 mL of n-hexane into 50 mL-Erlenmeyer flask.
8. Put them in rotary shaker with 150 rpm for 10 minutes.
9. After 10 minutes, pour all solutions into each test tube.
10. Left them until the solution separates into two layers.
11. Pipetted 1.5 mL of upper layer of solution into GC vial.
12. Analyzed concentration of sample by Gas Chromatography.

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Adsorbent characterization

All adsorbents (AC, HCl-AC and NaOH-AC) were pyrolysed in the furnace at 500°C with an absence of oxygen for 1 h in order to carbonize them into activated carbon. Since water hyacinth consists of 12-13% of lignin and NaOH could remove more lignin than HCl [30], the amount of NaOH-treated water hyacinth pyrolysed was less than that of activated carbon treated by other methods. Due to high temperature of pyrolysis, NaOH-treated water hyacinth was partly changed into ash as shown in Figure 4.1. Thus, NaOH-AC was not used to study its adsorption performance in this work. The characteristics of each adsorbent including carbon content, surface area and pore diameter are shown in Table 4.1. It can be seen that HCl treatment could improve the adsorbent characteristics comparing with untreated method. Taking into account the pore sizes of AC and HCl-AC comparing with the molecular diameter of atrazine which is 10.36 Å [29], it was clearly seen that both adsorbents could still adsorb atrazine from water effectively.

Figure 4.1 NaOH-AC after pyrolysed at 500°C for 1 hour.

Table 4.1 Characteristics of adsorbents.

Adsorbent type	**Carbon content (%)**	**Surface area (m^2/g)**	**Pore diameter (Å)**
AC	38.921	160.4	80.94
HCl-AC	71.192	436.0	29.01
NaOH-AC		Ash	

4.2 Study the effect of activated carbon preparation methods on adsorption efficiency

The comparison of AC and HCl-AC adsorption efficiencies was accomplished by using 0.1 g of each adsorbent to adsorb 12 ppm of atrazine solution until the equilibrium was reached. The changes of atrazine concentrations in solutions by AC and HCl-AC adsorptions were showed in Figures 4.2. From the result, the AC and HCl-AC reached the equilibrium in 240 and 300 minutes, respectively. Furthermore, their adsorption capacities and adsorption efficiencies were calculated to be 18.78 mg/g and 59.76% for AC and 23.54 mg/g and 75.58% for HCl-AC. These results could confirm that HCl-treated method could improve adsorbent characteristics which affected the increasing of capacity and efficiency of adsorption. Therefore, among these, HCl-AC was the best one for removing atrazine from water.

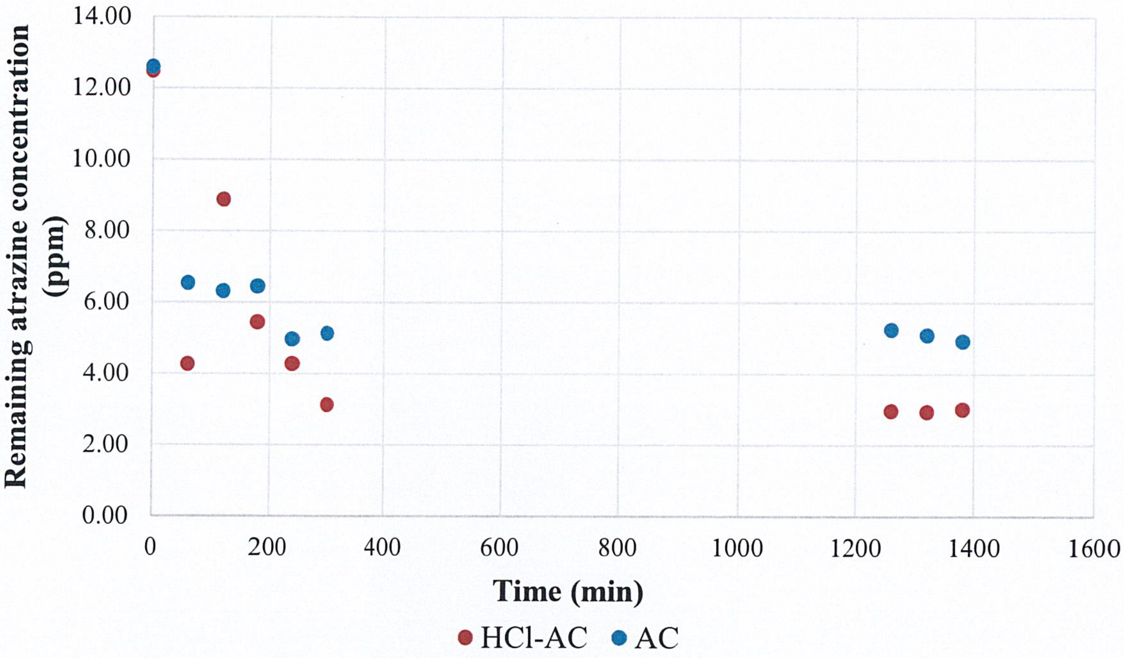

Figure 4.2 The changing of remained atrazine concentration by AC and HCl-AC adsorption.

4.3 Adsorption isotherm study

According to the higher surface area, adsorption capacity and adsorption efficiency of HCl-AC, so it was chosen to study the adsorption phenomenon by varying the initial atrazine concentrations in the range of 0-15 ppm. At the initial concentration of 3-6 ppm, HCl-AC could efficiently adsorb all atrazine in water, hence these data were omitted for identifying the adsorption isotherm. The data obtained from other initial concentrations were plotted to fit with 3 types of adsorption isotherm equations that were Langmuir, Freundlich, and Temkin equations which are shown in Figures 4.3 - 4.5, respectively. It can be seen that the adsorption isotherm of HCl-AC tended to fit Langmuir equation with the highest of R^2 value of 0.7512. This revealed that the atrazine adsorption by HCl-AC was chemical adsorption. Moreover, the value of energy of adsorption (K_L) and the maximum adsorption capacity of atrazine on HCl-AC (q_m) could be obtained from the graph which were 10.4615 L/mg and 24.5098 mg/g, respectively as shown Table 4.2. The dimensionless constant R_L can also be defined from a Langmuir equation which represents the separation factor of equilibrium parameter. The R_L value from this graph was 0.0065-0.0104 that means the adsorption of atrazine on HCl-AC was favorable.

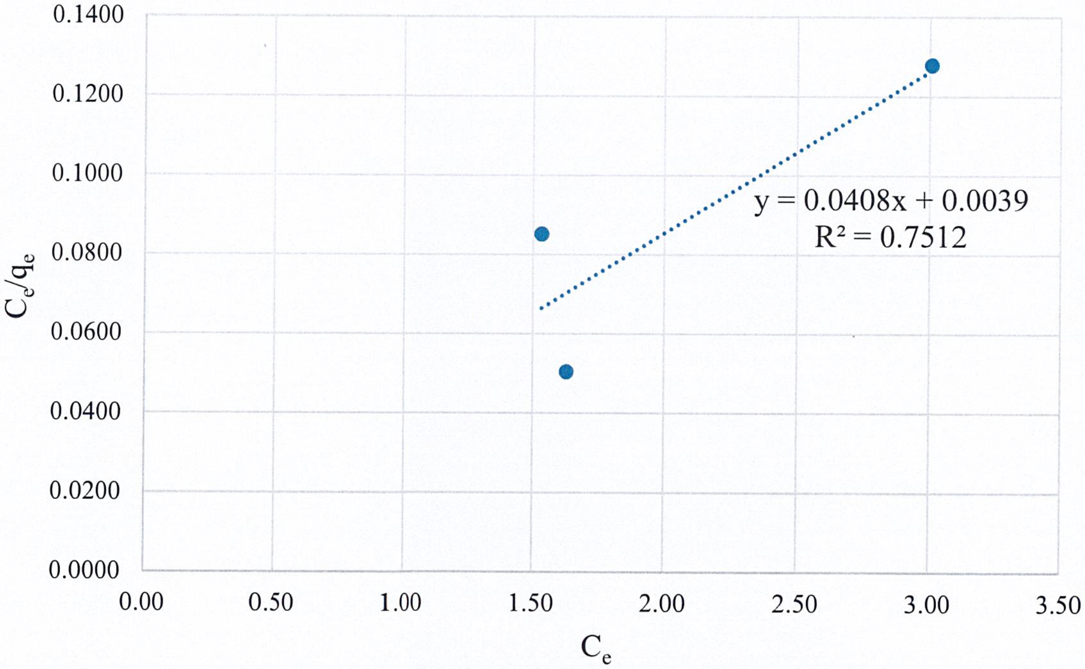

Figure 4.3 Langmuir isotherm for atrazine adsorption.

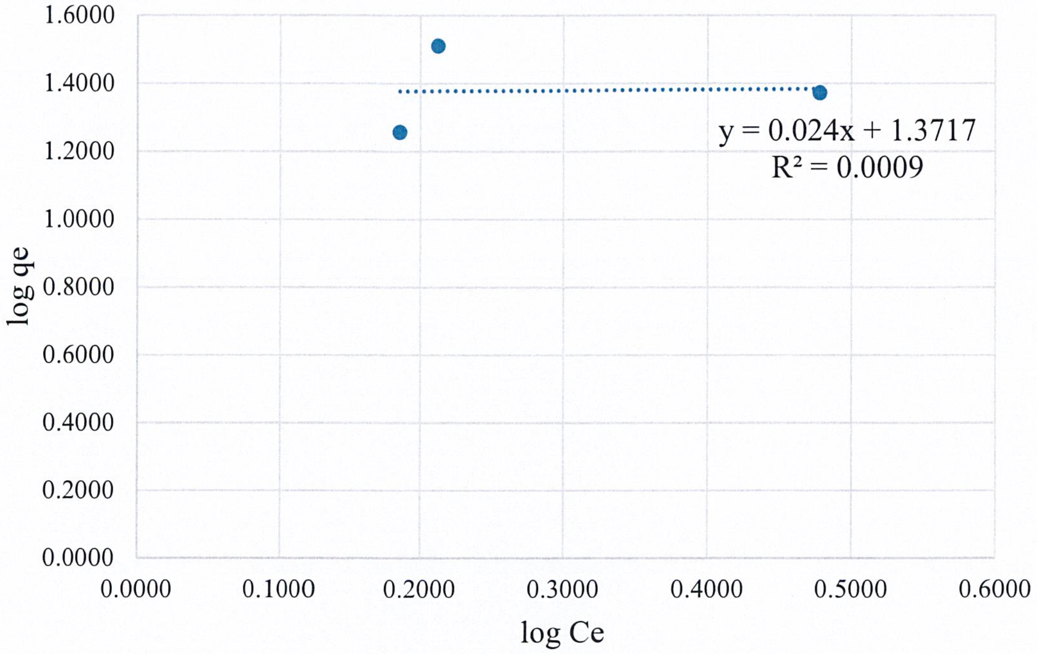

Figure 4.4 Freundlich isotherm for atrazine adsorption.

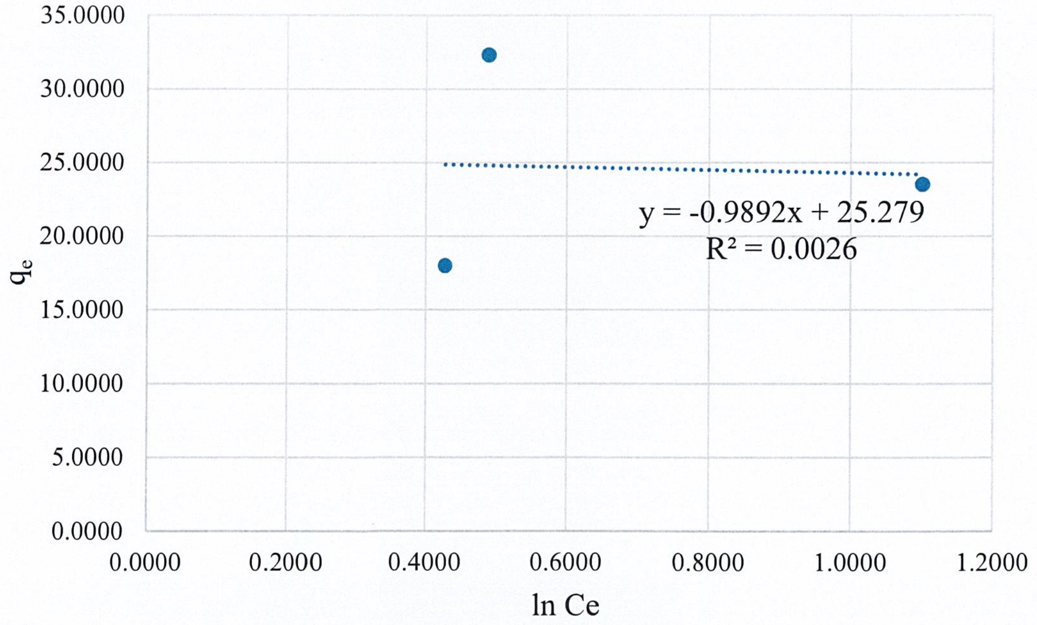

Figure 4.5 Temkin isotherm for atrazine adsorption.

Table 4.2 Parameters and R^2 values of Langmuir, Freundlich, and Temkin isotherms.

Langmuir isotherm			
q_m (mg/g)	**K_L (L/mg)**	**R_L**	**R^2**
24.5098	10.4615	0.0065-0.0104	0.7512
Freundlich isotherm			
1/n	**n**	**K_f (mg/g)**	**R^2**
0.0240	41.6667	23.5342	0.0009
Temkin isotherm			
A_T (L/mg)	**b_T (J/mol)**	**B**	**R^2**
0.0000	-2546.6458	-0.9892	0.0026

4.4 Adsorption kinetics study

Besides adsorption isotherm, HCl-AC was also chosen to study its kinetics of adsorption. The 0.1 g of adsorbent was used to adsorb 15 ppm of atrazine solution until the system reached its equilibrium. The samples of solution were collected in appropriate times and measured their concentrations by GC. From Figure 4.6, it can be observed that the equilibrium of adsorption was reached within 5 h. All collected data were plotted by 4 kinetics models that were Boyd, Weber and Morris, Pseudo-first-order and Pseudo-second-order kinetics models as shown in Figures 4.7 – 4.10, respectively. The kinetics of adsorption of HCl-AC tended to fit pseudo-second-order kinetics model with R^2 of 0.9806. Moreover, the q_e value for pseudo-second-order obtained from the graph was 33.00 mg/g and a kinetics constant (k_2) was 0.001475 g/ mg min as shown in Table 4.3. The results indicated that the adsorption phenomenon of HCl-AC was adsorption limit and two active sites of adsorbent were required to adsorb one molecule of atrazine.

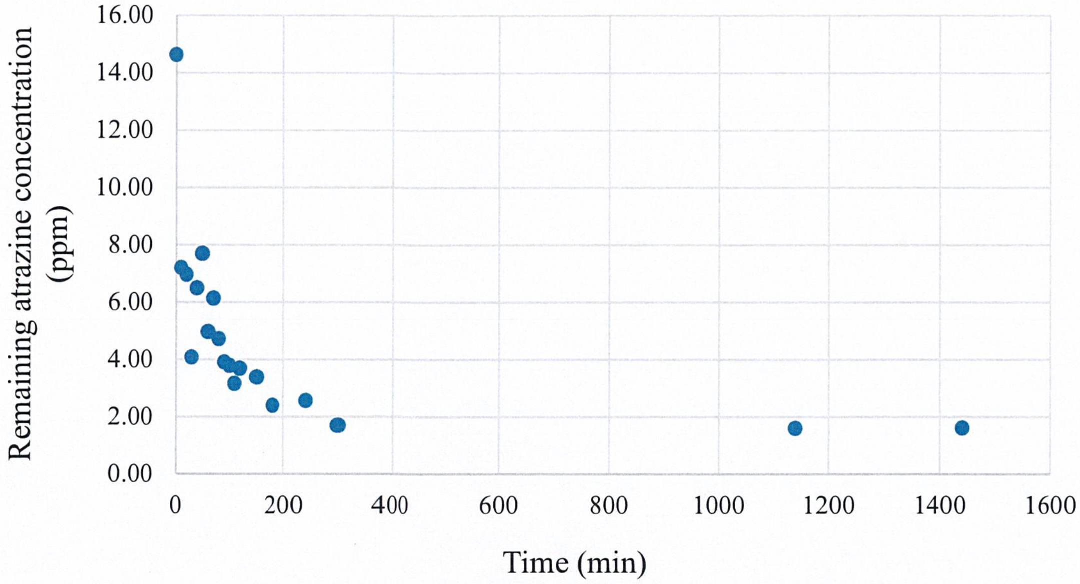

Figure 4.6 The changing of remaining atrazine concentration from 15 ppm by HCl-AC adsorption.

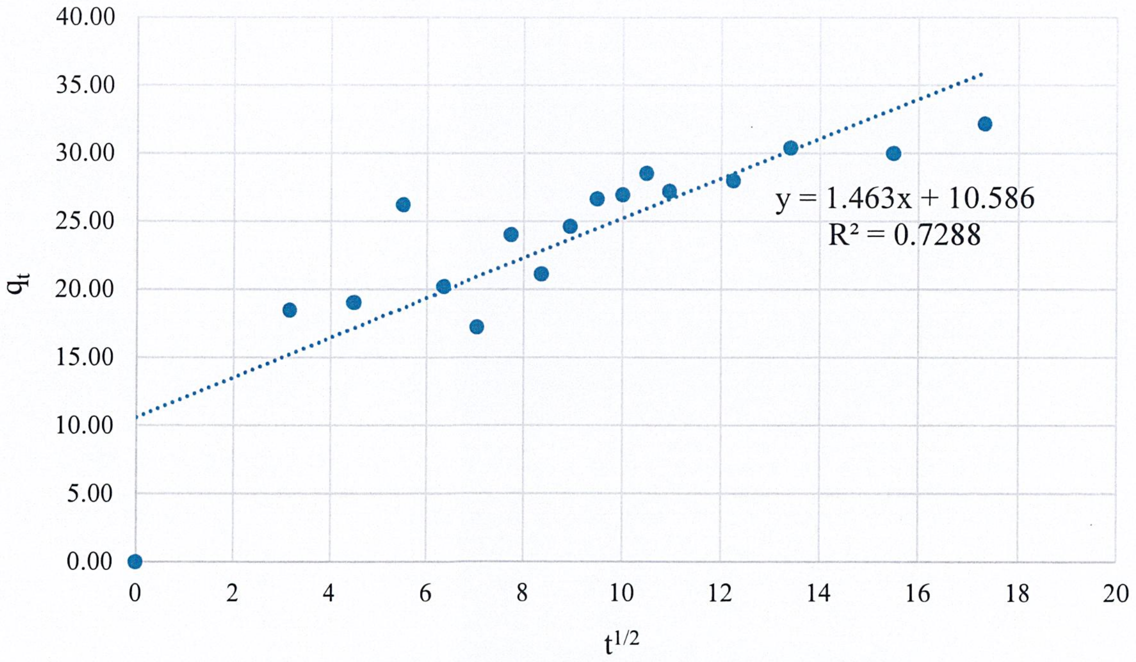

Figure 4.7 Boyd kinetics model for atrazine adsorption.

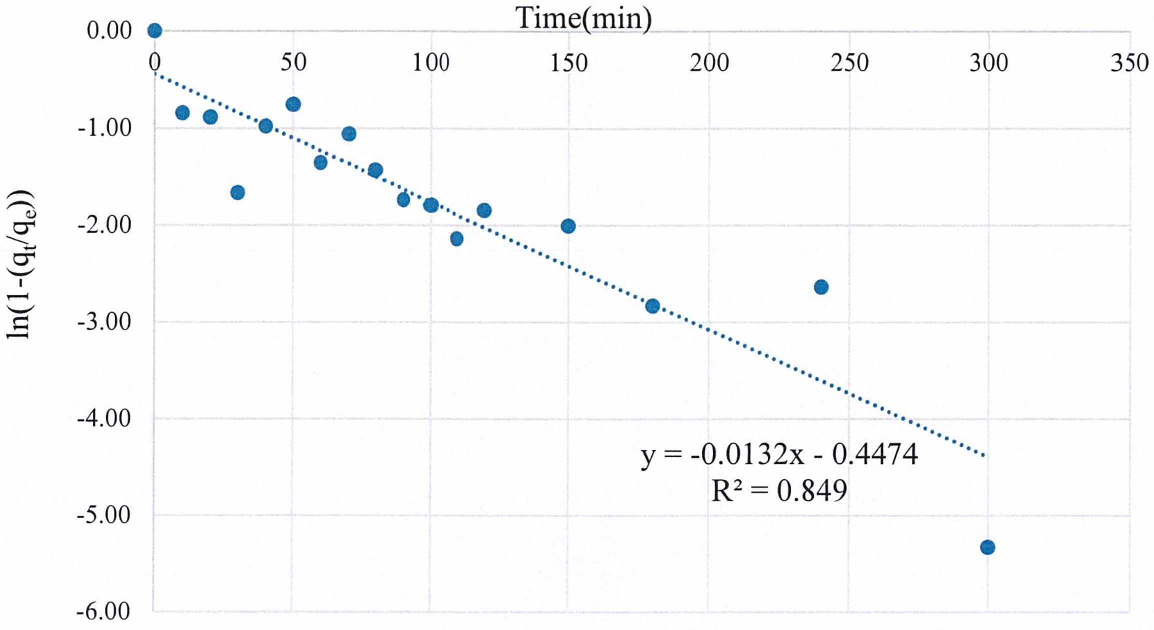

Figure 4.8 Weber and Morris kinetics model for atrazine adsorption.

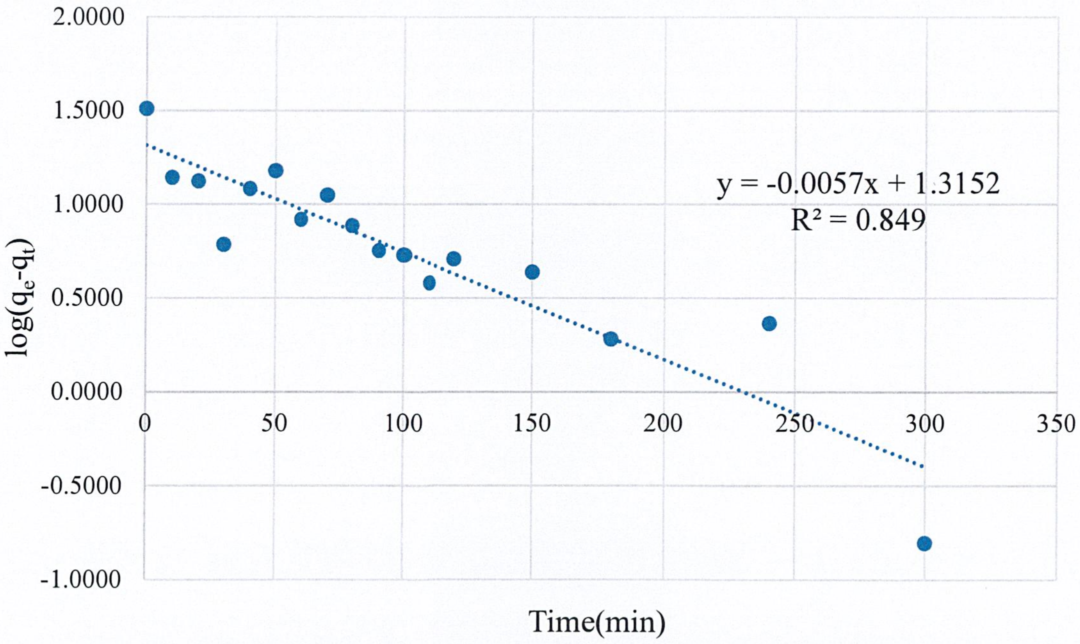

Figure 4.9 Pseudo-first-order kinetics model for atrazine adsorption.

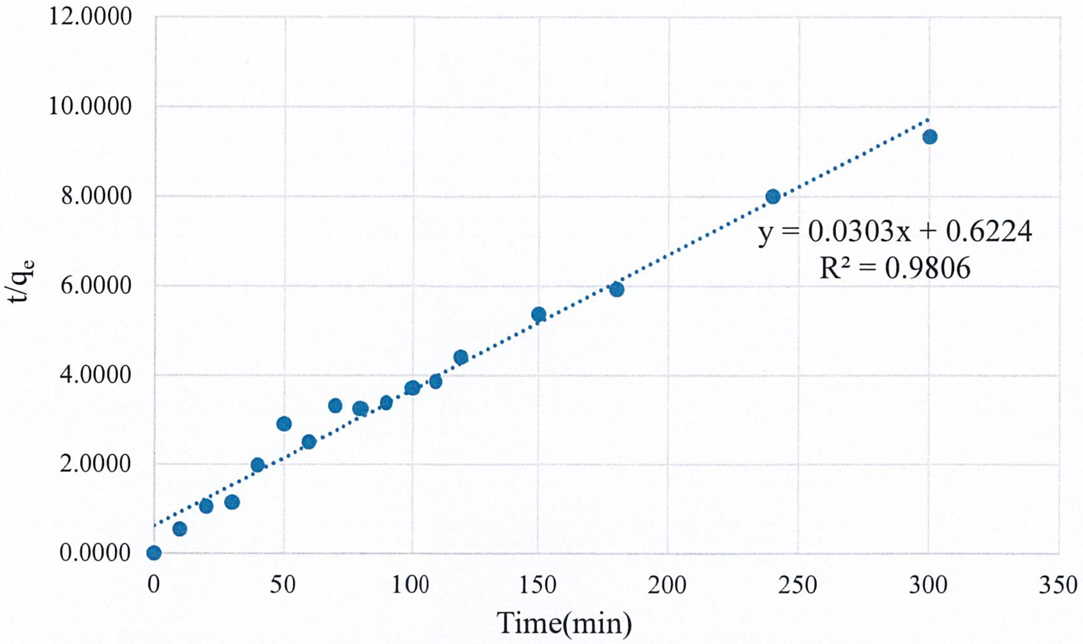

Figure 4.10 Pseudo-second-order kinetics model for atrazine adsorption.

Table 4.3 Parameters and R^2 values for Boyd, Weber and Morris, Pseudo-first-order and Pseudo-second-order kinetics models.

Boyd model		
	$\frac{D_s\pi^2}{r^2}$ **(1/min)**	R^2
	0.0132	0.8490
Weber and Morris model		
C (mg/g)	k_p **(mg/g min$^{1/2}$)**	R^2
10.5860	1.4630	0.7288
Pseudo-first-order model		
q_e **(mg/g)**	k_1 **(1/min)**	R^2
20.6633	0.0131	0.8490
Pseudo-second-order model		
q_e **(mg/g)**	k_2 **(g/mg min)**	R^2
33.0033	0.001475	0.9806

CHAPTER V
CONCLUSION AND SUGGESTIONS

5.1 Conclusion

The research of atrazine removal by an adsorbent synthesized from water hyacinth aims to find the suitable adsorbent preparation method for atrazine removal. There were 3 types of adsorbent synthesized in this work which were untreated (AC), HCl- treated (HCl-AC) and NaOH- treated (NaOH-AC) activated carbons. The experiments were performed to investigate the effect of different adsorbent preparation methods on adsorption efficiency and also determines the suitable adsorption isotherm and kinetics model of the best synthesized activated carbon for atrazine adsorption.

From the experiment, the best activated carbon preparation method for atrazine removal was HCl-AC. This method can improve adsorbent characteristics by increasing carbon content and surface area from 38.921% to 71.192% and 160.4 to 436.0 m^2/g, respectively. Moreover, its adsorption capacity and efficiency were increased from 18.78 mg/g to 23.54 mg/g and 59.76% to 75.58%, respectively. The adsorption experiments revealed that the phenomenon of atrazine adsorption by HCl-AC was chemical adsorption because its adsorption isotherm tended to fit Langmuir equation. In addition, this process was limited by adsorption (reaction limit) which needed two active sites to adsorb one molecule of atrazine because its kinetics of adsorption tended to fit Pseudo-second-order kinetics model.

5.2 Suggestions

5.2.1 Other adsorption affective factors should be studied for example the other type of adsorbent raw material with higher carbon content, other types of activated carbon preparation method or pH-value of solution.

5.2.2 For adapting to practical use, a continuous adsorption process should be studied.

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APPENDICES

APPPENDIX A
EXPERIMENTAL EQUIPEMENTS

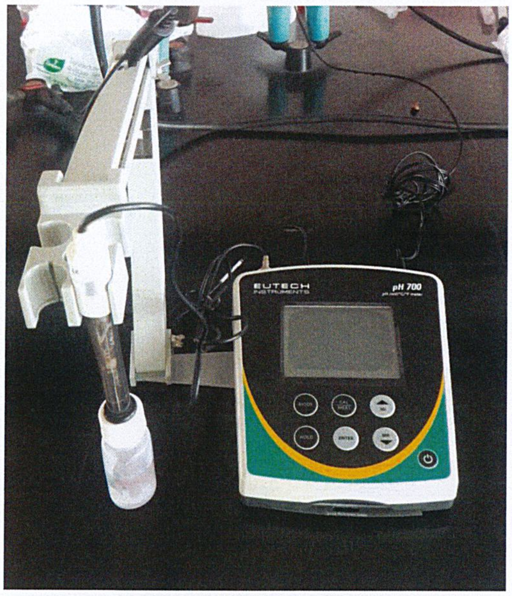

Figure A.1 pH-meter

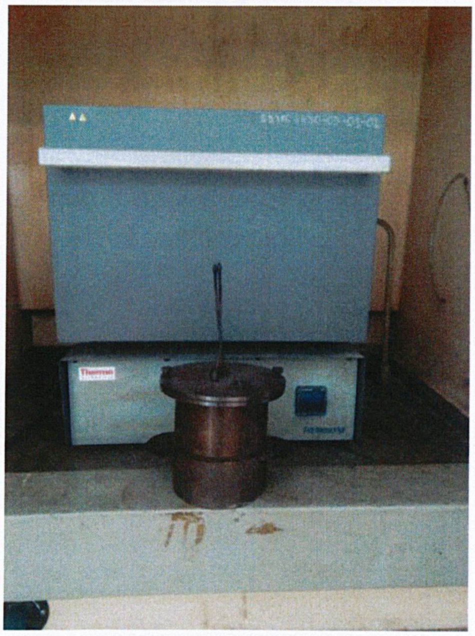

Figure A.2 Reactor and furnace for pyrolysis of water hyacinth.

Figure A.3 Sieve shaker.

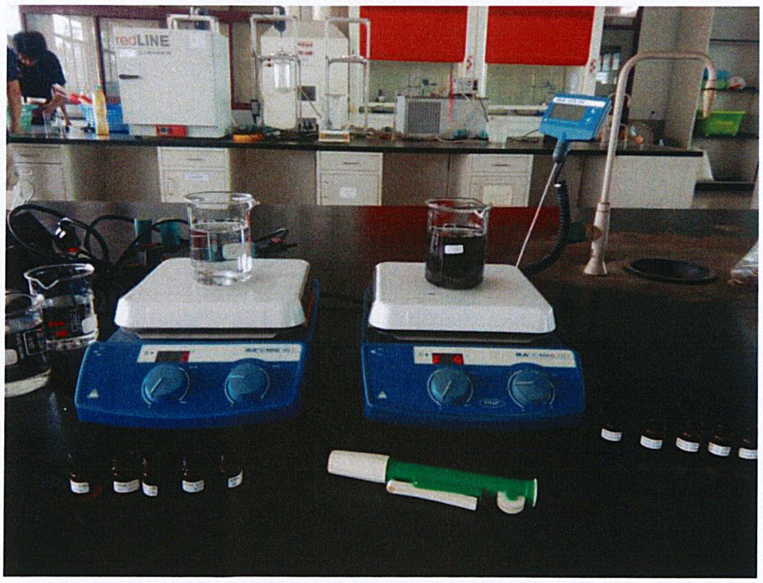

Figure A.4 Magnetic stirrer plate.

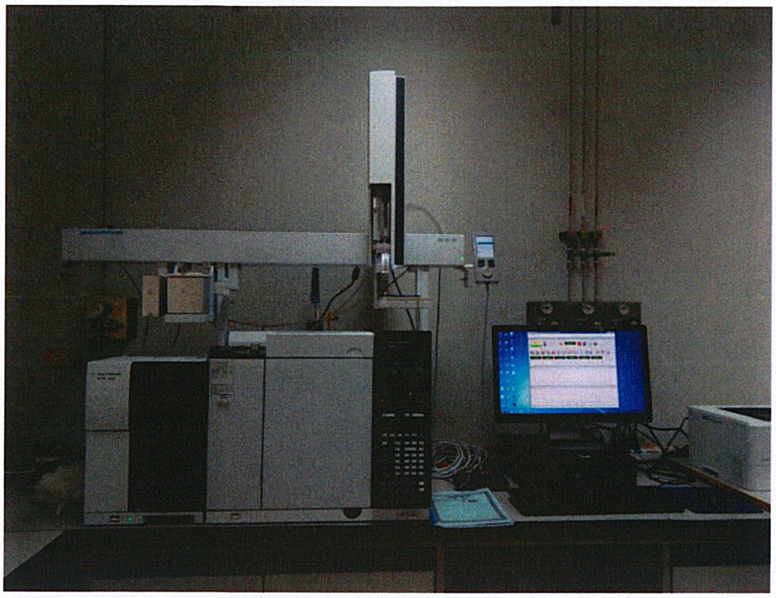

Figure A.5 Gas chromatography – Mass Spectroscopy (GC-MS).

APPENDIX B
ATRAZINE STANDARD CURVE

1. GC condition testing

Seven concentrations of atrazine solution were prepared for testing the GC analysis condition. . The 0.001 g. atrazine standard (analytical grade) was dissolved in 50 mL of n-Hexane to make 20 ppm of atrazine solution. Then, it was diluted to be 0, 3, 6, 9, 12 and 15 ppm by adding n-hexane. After that, 1.5 mL of all solutions were prepared in GC vails (3 vials for each concentration) and injected into GC to find the relationship between their concentrations and detected area under atrazine peak. The results are shown in Table B.1.

Table B.1. The results of GC detection for condition testing.

Atrazine concentration (ppm)	Area	Average
0	0	0
	0	
	0	
3	4049691	3719479
	3693469	
	3415276	
6	8176086	9049823
	8861098	
	10112284	
9	11411515	11743770
	12426516	
	11393278	
12	16054509	16425247
	16181837	
	17039395	
15	22697313	22912107
	23377826	
	22661182	
20	33633250	27877634
	24351588	
	25648065	

Then, the standard curve which shows the relationship between concentration and area was plotted in Figure B.1.

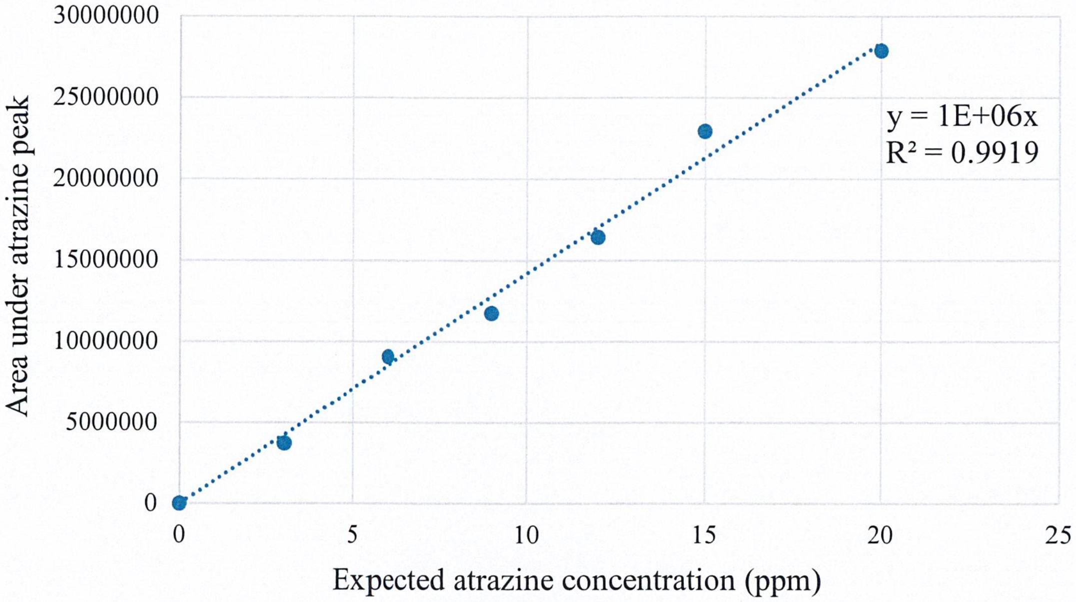

Figure B.1 Atrazine standard curve for GC condition testing.

This graph could confirm that the condition that used to detect atrazine was acceptable because it could find and detect the atrazine. Furthermore, the results of detecting area were increased when the atrazine concentration increase and it could also plot into linear with R^2 was 0.9919 which was acceptable to be a standard curve.

2. Standard curve

As this project aims to remove atrazine from water therefore, the standard curve preparation was necessary to be prepared with the same method for experiment that means the 0.001 g of atrazine should be dissolved in 50 mL of distilled water and diluted to be 0, 3, 6, 9, 12 and 15 ppm. Then, 1 mL of each concentration was added to 50mL-Erlenmeyer flask, then 2 mL of n-hexane was added into each flask. After that, all flasks were stirred in rotary shaker with 150 rpm for 10 minutes in order to extract atrazine from water. After 10 minutes, the solution were poured into test tube and left until it separated into 2 layers. The top layer which was the layer of n-hexane was separated into GC vials and injected into GC to find the relationship between their concentrations and detected area under atrazine peak (each concentration was prepared three times for three vials). The results are shown in Table B.2 for isotherm study and Table B.3 for kinetics study.

Table B.2 The results of GC detection to plot standard curve for isotherm study.

Atrazine concentration (ppm)	Area	Average
0	0	0
	0	
	0	
3	749450	827302
	738874	
	993583	
6	2061008	2016118
	2391173	
	1596172	
9	3299076	3693386
	3566449	
	4214633	
12	6319285	6298646
	6091315	
	6485337	
15	7766492	7537391
	7382937	
	7462745	
20	11551834	12070343
	12687041	
	11972154	

Table B.3 The results of GC detection to plot standard curve for kinetics study.

Atrazine concentration (ppm)	**Area**	**Average**
0	0	0
	0	
	0	
3	415428	389507
	363587	
	284589	
6	615396	613583
	611770	
	638673	
9	963740	951877
	940015	
	920508	
12	1587981	1573604
	1559226	
	1414257	
15	2611592	2656852
	2833774	
	2702112	
20	3000811	3139815
	3278818	
	2797446	

Then, the results were plot into graph to show the relationship between atrazine concentrations and detecting area under the atrazine peak which are shown in Figure B.2 and Figure B.3. Both graphs had R^2 value of 0.9364 and 0.9429, respectively. Even through, the R^2 values were less than R^2 value of standard curve for GC condition testing because it was affected from the matrix (sample preparation method) but they were still acceptable (acceptable R^2 value for standard curve is more than 0.85).

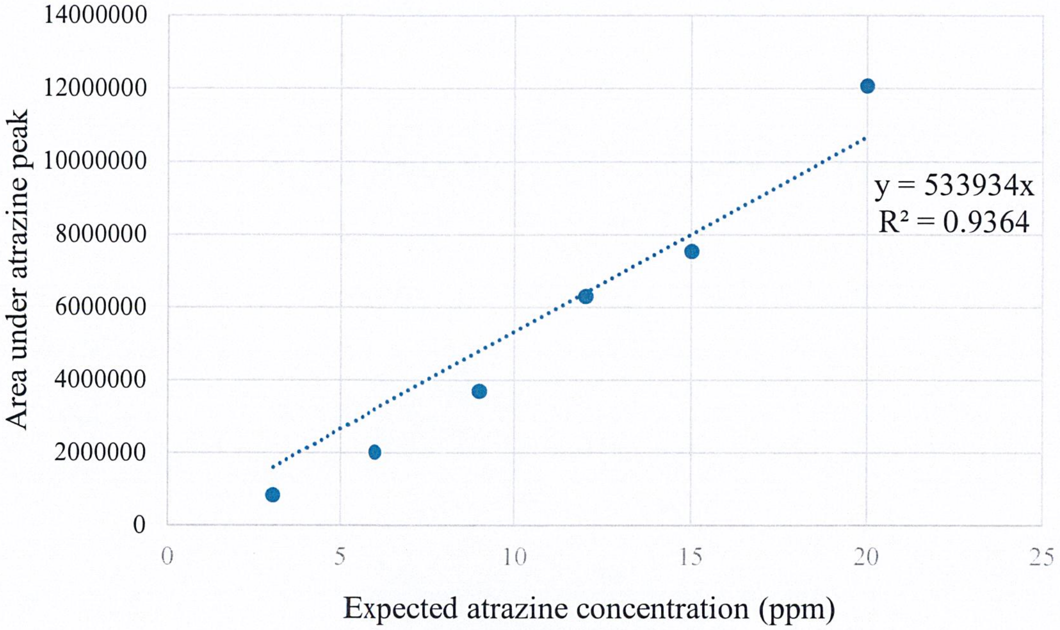

Figure B.2 Atrazine standard curve for isotherm study.

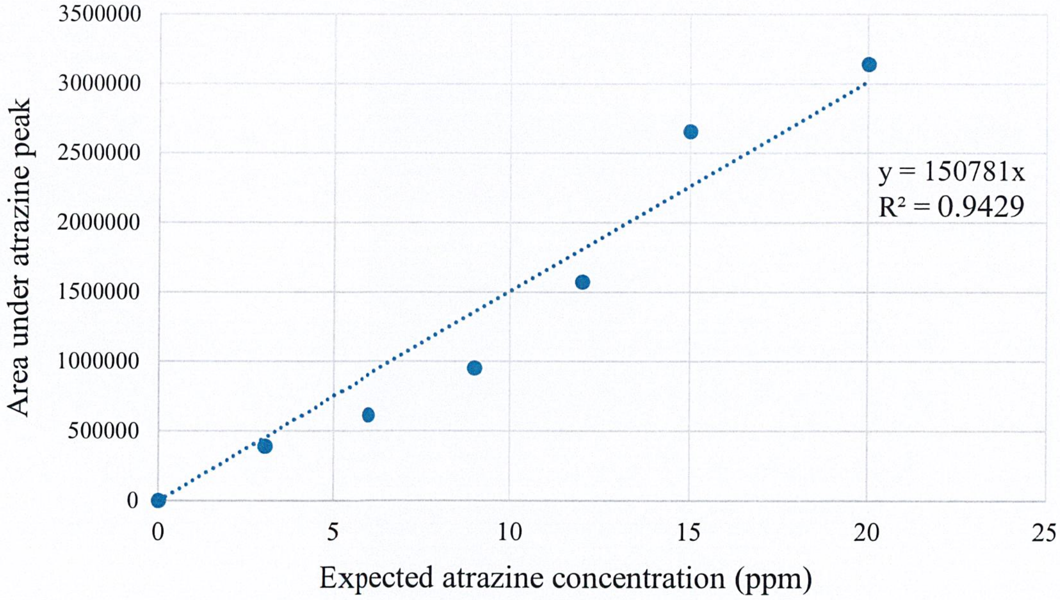

Figure B.3 Atrazine standard curve for kinetics study

3. Method of validation [35]

The method of validation is the process used to confirm that the analytical procedure is suitable for its intended use. The results from method of validation can be used to judge the quality, reliability and consistency of analytical results.

The method was begun by injecting 2 atrazine concentrations which were 5 and 14 ppm (using hexane extraction method for preparing the samples). Each concentration was prepared into 10 vials separately. After injection, the results were calculated into concentration value by using equation from standard curve. Then, all values were used to validate by Precision and Accuracy method.

3.1 Precision

Precision of analytical method is generally evaluated by calculating relative standard deviation (RSD) of a set of data from Equation B.1.

$$RSD = \frac{SD}{Mean} \times 100 \qquad \text{(B.1)}$$

Precision of GC method was checked to assess the reproducibility of instrument response to target of sample. In order to assess the analytical method precision, measurements were done under conditions of repeatability. Repeatability was evaluated by measuring 10 atrazine solution spiked with 5 and 14 ppm. The results are shown Table B.4.

Table B.4 RSD value for GC detecting method.

Spike (ppm)	Detected atrazine concentration (ppm)	RSD value
5	3.31	7.1074
	3.52	
	4.14	
	3.51	
	3.82	
	4.20	
	3.84	
	3.93	
	3.42	
	4.37	
14	15.34	9.4748
	15.02	
	12.91	
	13.66	
	14.10	
	15.33	
	13.33	
	12.68	
	13.52	
	14.84	
	15.34	

The RSD acceptable value is less than 10 and the value of RSD were 7.1074 and 9.4748 therefore, this analytical method is suitable for atrazine detection.

3.2 Accuracy

Accuracy of analytical method is evaluated by calculating the %recovery of a set of data from Equation B.2.

$$\%Recovery = \frac{Measured\ value}{Exact\ value} \times 100 \qquad \text{(B.2)}$$

The measurements were also done under conditions of repeatability. An acceptable value of % recovery for organochloride pesticide should be in range of 60-120%. From the results in Table B.5, the %recovery value of both 5 and 14 ppm were in between 60-120% with the value of 78.32% and 100.63%. Therefore, the developed method was accurate for quantification of atrazine.

Table B.5 %Recovery of GC detecting method.

Spike (ppm)	Detected atrazine concentration (ppm)	%Recovery	Average of %Recovery
5	3.31	91.02	78.32
	3.52	94.72	
	4.14	105.64	
	3.51	94.64	
	3.82	99.99	
	4.20	106.83	
	3.84	100.39	
	3.93	102.04	
	3.42	93.10	
	4.37	109.8009	
14	15.34	108.22	100.63
	15.02	106.22	
	12.91	92.92	
	13.66	97.67	
	14.10	100.41	
	15.33	108.17	
	13.33	95.58	
	12.68	91.47	
	13.52	96.81	
	14.84	105.09	
	15.34	108.22	

APPENDIX C
EXPERIMENTAL DATA OF ADSORPTION EXPERIMENT

1. Study the effect of activated carbon preparation method on adsorption efficiency

The 12 ppm of atrazine solution were adsorbed by AC and HCl-AC in order to compare their adsorption capacities and adsorption efficiencies. The adsorption processes were left until they reached the equilibrium. The samples were collected every hour and measured the remaining atrazine concentration by GC. Each sample was injected into GC for 2-3 times in order to decrease the possibility of error from GC detection. All measured results of both AC and HCl-AC adsorptions are shown in Table C.1.

Table C.1. Raw data from GC measurement for studying the effect of activated carbon preparation method on adsorption efficiency.

Time (min)	AC		HCl-AC	
	Area under atrazine peak from GC measurement	**Calculated concentration (ppm)**	**Area under atrazine peak from GC measurement**	**Calculated concentration (ppm)**
0	6860291	12.85	6310457	11.82
	6980123	13.07	7216215	13.52
	6762195	12.66	6474386	12.13
60	3757703	7.04	2442126	4.57
	3226183	6.04	2346420	4.39
	-	-	2038900	3.82
120	3655179	6.85	5075453	9.51
	3261054	6.11	4405505	8.25
	3198966	5.99	4743339	8.88
180	3467203	6.49	3106572	5.82
	3418680	6.40	2707516	5.07
240	2844505	5.33	2244367	4.20
	2611108	4.89	2316644	4.34
	2764945	5.18	-	-
300	3076822	5.76	1606856	3.01
	2575503	4.82	1729173	3.24
	2878679	5.39	-	-
1260	2920766	5.47	1551781	2.91
	2932993	5.49	1612247	3.02
	2550555	4.78	-	-
1320	2729459	5.11	1597635	2.99
	2846314	5.33	1513513	2.83
	2577926	4.83	1588216	2.97
1380	2628775	4.92	1583972	2.97
	2422664	4.54	1626534	3.05
	2831689	5.30	-	-

The average values of concentration of each time are plotted to describe the change of remaining atrazine concentration, as shown in Figures C.1 and C.2, of adsorption by AC and HCl-AC, respectively.

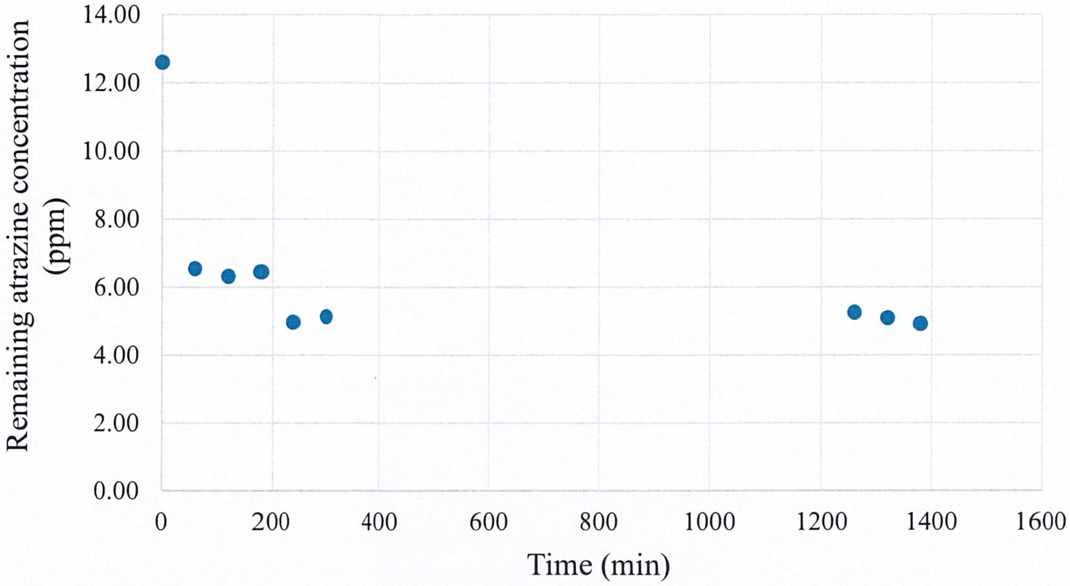

Figure C.1 The changing of remaining atrazine concentration by time of 12 ppm for adsorption by AC.

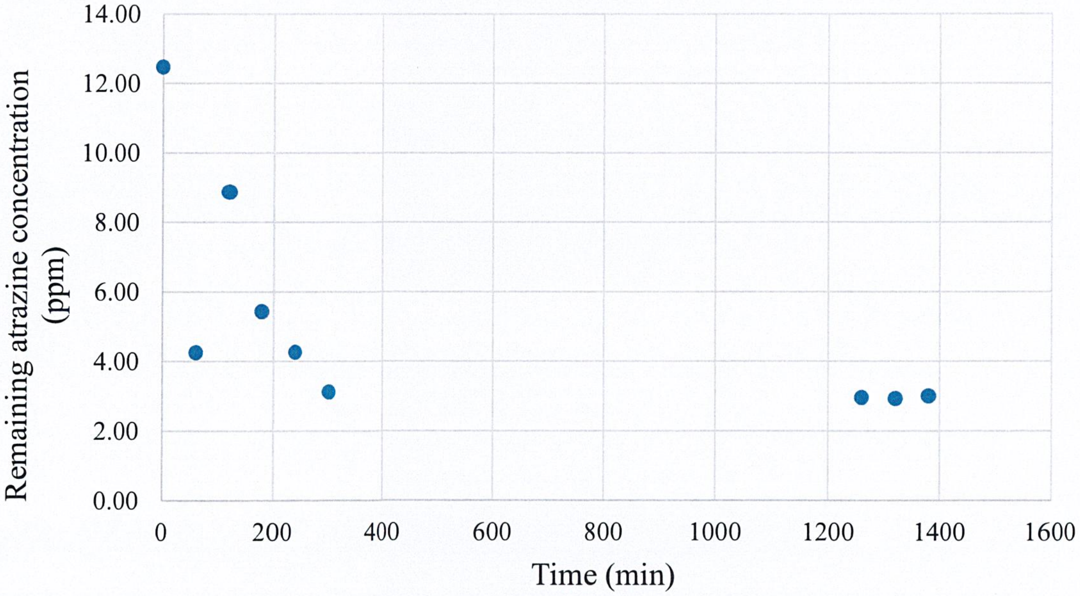

Figure C.2 The changing of remaining atrazine concentration by time of 12 ppm for adsorption by HCl-AC.

2. Adsorption isotherm study

The initial atrazine concentration was varied in a range of 0-15 ppm in order to study the isotherm of adsorption. The solution samples were collected every hour until the systems reached their equilibriums and were measured the concentrations by GC. Each sample was injected and measured by GC for 2-3 times in order to decrease the error from GC detection.

Table C.2 shows the raw data in term of area under the atrazine peak from GC measurement of each concentration and the calculated concentration value by using equation from standard curve.

Table C.2 Raw data from GC measurement for adsorption isotherm study.

Expected initial concentration (ppm)	Time (min)	Area under atrazine peak from GC measurement	Calculated concentration (ppm)
3	0	1548934	2.90
		1434680	2.69
	60	370905	0.69
		343922	0.64
	120	0	0.00
		240405	0.45
	180	0	0.00
		0	0.00
9	0	5144205	9.63
		4644336	8.70
		4729755	8.86
	60	2361847	4.42
		2087936	3.91
		2434358	4.56
	120	1386522	2.60
		1359099	2.55
		1272013	2.38
	180	782711	1.47
		840456	1.57
		795649	1.49
	240	855206	1.60
		792708	1.48
		847446	1.59
12	0	6310457	11.82
		7216215	13.52
		6474386	12.13
	60	2442126	4.57
		2346420	4.39
		2038900	3.82
	120	5075453	9.51
		4405505	8.25

		4743339	8.88
	180	3106572	5.82
		2707516	5.07
	240	2244367	4.20
		2316644	4.34
	300	1606856	3.01
		1729173	3.24
	1260	1551781	2.91
		1612247	3.02
	1320	1597635	2.99
		1513513	2.83
		1588216	2.97
	1380	1583972	2.97
		1626534	3.05
15	0	2227740	14.77
		2196197	14.57
		2366212	15.69
	60	791354	5.25
		762185	5.05
		695441	4.61
	120	516187	3.42
		592442	3.93
		559194	3.71
	180	355988	2.36
		349549	2.32
		379472	2.52
	240	413730	2.74
		320944	2.13
		424179	2.81
	300	241811	1.60
		256875	1.70
		267550	1.77
	1140	247721	1.64
		238013	1.58
		235003	1.56
	1440	239481	1.59
		262037	1.74
		224699	1.49

The adsorption phenomena of each concentration are shown in terms of average remaining atrazine concentrations by time in Figures C.3 - C.6 which represents 3, 9, 12 and 15 ppm of atrazine initial concentration respectively.

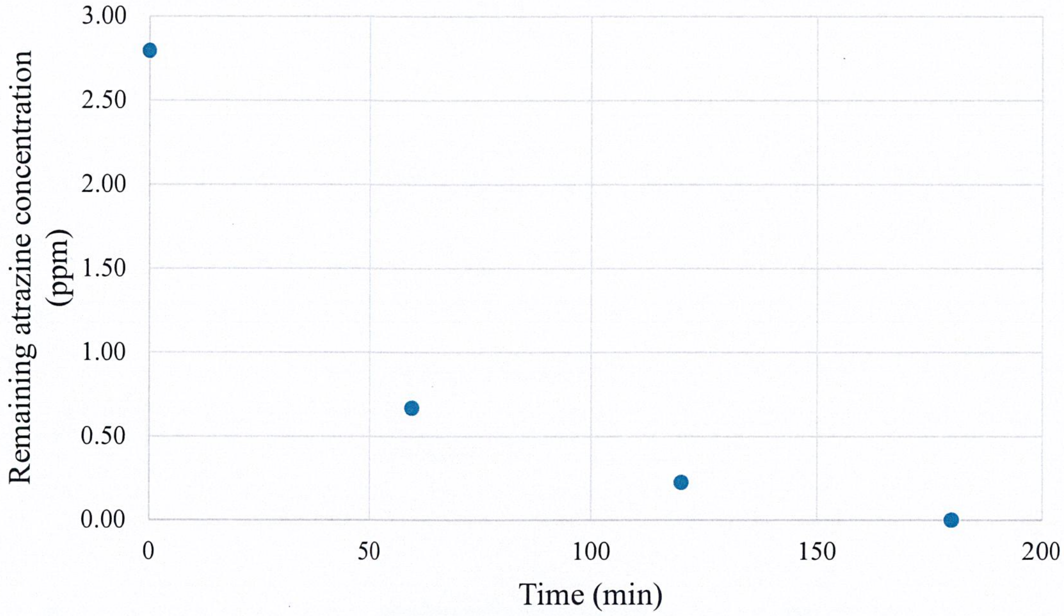

Figure C.3 The changing of remaining atrazine concentration by time of 3 ppm of initial concentration.

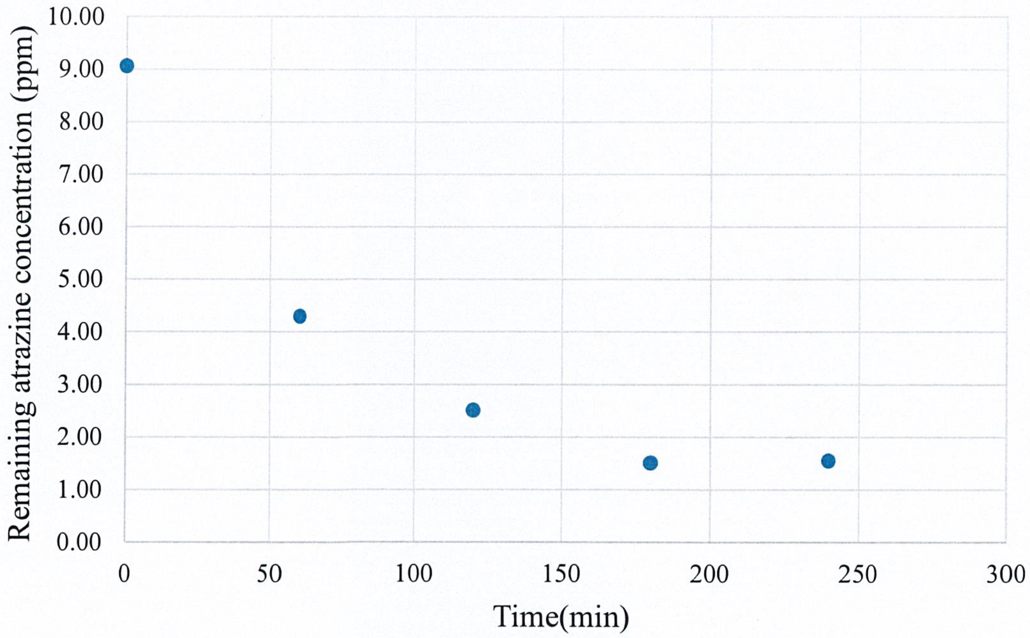

Figure C.4 The changing of remaining atrazine concentration by time of 9 ppm of initial concentration.

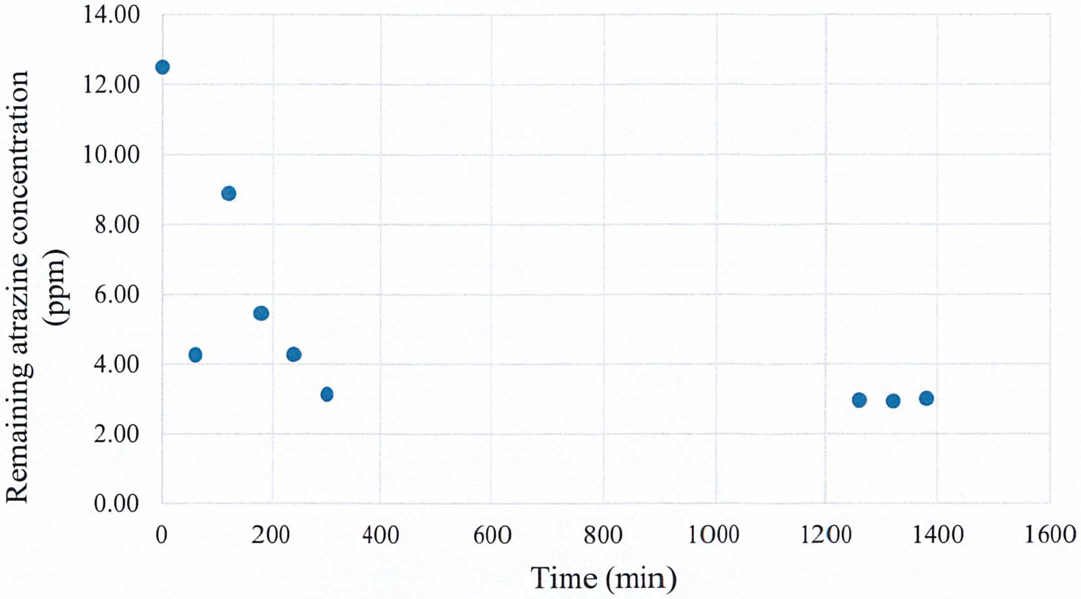

Figure C.5 The changing of remaining atrazine concentration by time of 12 ppm of initial concentration.

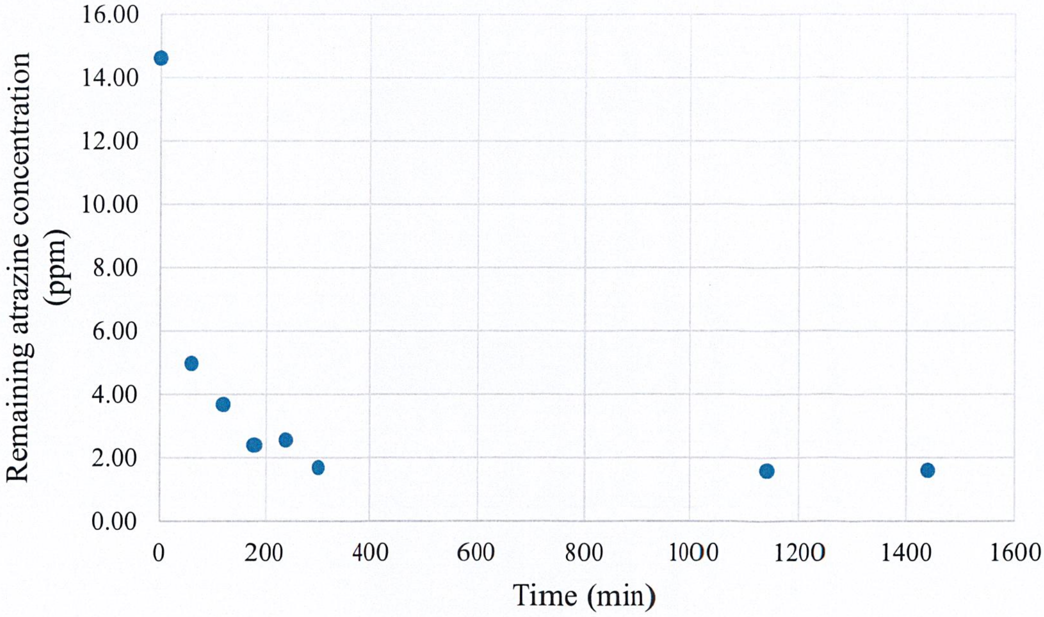

Figure C.6 The changing of remaining atrazine concentration by time of 15 ppm of initial concentration.

This work used 4 types of adsorption isotherm models to study the adsorption phenomenon of atrazine by HCl-AC that were Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The adsorption isotherm graphs were plotted by using the average value of initial concentrations and equilibrium concentrations from raw data in Table C.2 to calculate other parameters. The common parameters are shown in Table C.3 which consists of average initial concentrations or C_0 (ppm), adsorbent weight (g), average equilibrium concentrations or C_e (ppm), and amount of adsorbed or q_e (mg/g).

Table C.3 Common parameters of isotherm study.

Initial concentration (ppm)	**Adsorbent weight (g)**	**q_e (mg/g)**	**C_e (ppm)**
0	0	0	0
2.79	0.1032	6.7684	0.00
9.06	0.1045	18.0138	1.53
12.49	0.1008	23.5114	3.01
14.63	0.1005	32.3163	1.63

Each model has different of x- and y-axis parameters in order to plot the linear form of graph. The x-axis and y-axis values of every model are shown in Table D.4.

Table C.4 X-axis and Y-axis values for Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm model.

Langmuir isotherm		**Freundlich isotherm**	
X-axis (C_e)	**Y-axis (C_e/q_e)**	**X-axis (log C_e)**	**Y-axis (log q_e)**
1.53	0.0852	0.1858	1.2556
3.01	0.1279	0.4781	1.3713
1.63	0.0504	0.2122	1.5094

Temkin isotherm	
X-axis (log C_e)	**Y-axis (q_e)**
0.4278	18.0138
1.1009	23.5114
0.4886	32.3163

3. Adsorption kinetics study

The 15 ppm of atrazine concentration was prepared to study adsorption kinetics of HCl-AC. The solution samples were collected at 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 150, 180, 240, 300, 1140, and 1440 min. Every samples were injected and measured the concentration by GC for 3 times in order to decrease the possibility of the error of GC detection. The raw data are shown in Table C.5.

Table C.5 Raw data from GC measurement for adsorption kinetics study.

Time (min)	Area under atrazine peak from GC measurement	Calculated concentration (ppm)
0	2227740	14.77
	2196197	14.57
	2366212	15.69
10	1376000	9.13
	1092311	7.24
	1088435	7.22
20	985883	6.54
	1100872	7.30
	1067490	7.08
30	654299	4.34
	569715	3.78
	623623	4.14
40	887497	5.89
	1066083	7.07
	987027	6.55
50	1243243	8.25
	1092114	7.24
	1150300	7.63
60	791354	5.25
	762185	5.05
	695441	4.61
70	921253	6.11
	965336	6.40
	887975	5.89
80	754369	5.00
	674173	4.47
	708980	4.70
90	562634	3.73
	594666	3.94
	611536	4.06
100	502527	3.33
	611733	4.06
	598810	3.97

110	511572	3.39
	472876	3.14
	445933	2.96
120	516187	3.42
	592442	3.93
	559194	3.71
150	539047	3.58
	579669	3.84
	410195	2.72
180	355988	2.36
	349549	2.32
	379472	2.52
240	413730	2.74
	320944	2.13
	424179	2.81
300	241811	1.60
	256875	1.70
	267550	1.77
1140	247721	1.64
	238013	1.58
	235003	1.56
1440	239481	1.59
	262037	1.74
	224699	1.49

There were 4 types of kinetics models used in this study which were Boyd, Weber and Morris, Pseudo-first-order and Pseudo-second-order kinetics model. All adsorption kinetics graphs were plotted by using the average value of concentrations in each time and equilibrium concentrations from raw data in Table C.5 to calculate parameter values for x-axis and y-axis. The common parameter values for plotting kinetics graph and values of both axis of every model are shown in Tables C.6 and C.7, respectively.

Table C.6 Common parameter values for kinetics study.

Time (min)	Average concentration at time t	Amount of adsorbed at each time (mg/g)	Average amount of adsorbed at equilibrium (mg/g)
0	14.63	0.00	32.32
10	7.21	18.46	
20	6.97	19.04	
30	4.08	26.22	
40	6.50	20.21	
50	7.71	17.22	
60	4.97	24.02	
70	6.13	21.13	
80	4.73	24.63	
90	3.91	26.66	
100	3.79	26.96	
110	3.16	28.52	
120	3.69	27.21	
150	3.38	27.97	
180	2.40	30.41	
240	2.56	30.01	
300	1.69	32.17	
1140	1.59	32.42	
1440	1.61	32.39	

Table C.7 X-axis and Y-axis values for Boyd, Weber and Morris, Pseudo-first-order and Pseudo-second-order kinetics model.

Boyd kinetics model		**Weber and Morris kinetics model**	
X-axis (t)	**Y-axis (ln(1-(q_t/q_e)))**	**X-axis ($t^{1/2}$)**	**Y-axis (q_t/q_e)**
0	0.0000	0	0.0000
10	-0.8467	3.1623	0.5712
20	-0.8892	4.4721	0.5890
30	-1.6673	5.4772	0.8112
40	-0.9818	6.3246	0.6254
50	-0.7607	7.0711	0.5327
60	-1.3586	7.7460	0.7430
70	-1.0602	8.3666	0.6536
80	-1.4352	8.9443	0.7619
90	-1.7409	9.4868	0.8246
100	-1.7965	10.0000	0.8341
110	-2.1388	10.4881	0.8822
120	-1.8440	10.9545	0.8418
150	-2.0058	12.2474	0.8654
180	-2.8292	13.4164	0.9409
240	-2.6364	15.4919	0.9284
300	-5.3292	17.3205	0.9952
Pseudo-first-order kinetics model		**Pseudo-second-order kinetics model**	
X-axis (t)	**Y-axis (log(q_e-q_t))**	**X-axis (t)**	**Y-axis (t/q_t)**
0	1.5095	0	0
10	1.1418	10	0.0000
20	1.1233	20	0.5416
30	0.7854	30	1.0505
40	1.0831	40	1.1441
50	1.1791	50	1.9789
60	0.9195	60	2.9040
70	1.0491	70	2.4984
80	0.8862	80	3.3134
90	0.7534	90	3.2483
100	0.7293	100	3.3765
110	0.5806	110	3.7090
120	0.7087	120	3.8575
150	0.6384	150	4.4101
180	0.2808	180	5.3621
240	0.3645	240	5.9183
300	-0.8049	300	7.9978

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