ACTIVATED CARBON FROM MANGROVE BY MICROWAVE IRRADIATION FOR ADSORPTION OF LEAD(II) IONS

by

TIMOTHY STEPHEN RAJ A/L PAUL

UNIVERSITI SAINS MALAYSIA

2022

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

2022

ACKNOWLEDGEMENT

I want to offer my heartfelt gratitude to those who made it possible for me to finish my report. Aside from fulfilling the requirements for a Bachelor of Chemical Engineering degree, this project represents a defining moment in my journey as an engineering student. This project bridges the gap between theory-based learning and skills-based learning by integrating the knowledge gained over the years and proving my ability by applying the knowledge.

A special gratitude I give to my supervisor Associate Professor Dr. Ridzuan Zakaria for guiding me in completing my final year project. His enthusiasm, incisive remarks, and useful knowledge assist me at all times in my research and thesis writing. His role in overseeing my progress made the project achievable. Moreover, I want to acknowledge with much gratitude the important role of the course coordinator, Professor Dr. Mohd Roslee Othman for his invaluable help in stimulating suggestions and knowledge throughout the course.

I owe School of Chemical Engineering a huge debt of gratitude for allowing me to use the facilities in completing my project. The technical staffs and colleagues deserve special recognition for their encouragement, direction and kind assistance, as well as intelligent remarks and recommendations which have made my project a success. I want to thank everyone again, including those I may have forgotten to mention but who assisted me directly or indirectly in accomplishing the project.

Timothy Stephen Raj A/L Paul

June 2022

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LIST OF SYMBOLS

Symbol	**Description**	**Unit**
$1/n_F$	Freundlich heterogeneity factor	-
C_e	Concentration of adsorbate solution at equilibrium	mg/L
C_o	Initial concentration of adsorbate solution	mg/L
C_t	Concentration of adsorbate solution at time, t	mg/L
K_C	Equilibrium constant	-
K_F	Freundlich constant	-
K_L	Langmuir constant	-
k_1	Rate constant of PFO	min^{-1}
k_2	Rate constant of PSO	g/mg.min
M_1	Concentration of stock solution	mg/L
M_2	Concentration of adsorbate solution	mg/L
Q_m	Maximum adsorption capacity	mg/g
q_e	Adsorption capacity at equilibrium	mg/g
q_t	Adsorption capacity at time, t	mg/g
R	Gas constant	kJ/mol.K
R^2	Correlation coefficient	-
R_L	Separation factor	-
T	Temperature	K
t	Contact time	min
V	Volume of solution	L
V_1	Volume of stock solution	L
V_2	Volume of adsorbate solution	L

W	Weight of adsorbent	g
%R	Removal percentage of metal ions	%
Δq	Deviation in adsorption capacity	%
ΔG^o	Gibbs energy	kJ/mol
ΔH^o	Enthalpy change	kJ/mol
ΔS^o	Entropy change	kJ/mol.K

LIST OF ABBREVATIONS

Symbol	**Description**
AC	Activated Carbon
CCD	Central Composite Design
CHNS	Carbon Hydrogen Nitrogen Sulphur
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared
PFO	Pseudo First Order
PSO	Pseudo Second Order
RSM	Response Surface Methodology
SGDs	Sustainable Development Goals
WHO	World Health Organization

KARBON TERAKTIF DARIPADA BAKAU MENGGUNAKAN PEMANASAN GELOMBANG MIKRO UNTUK PENYERAPAN ION PLUMBUM(II)

ABSTRAK

Plumbum adalah logam berat yang bertoksik dan merupakan sumber pencemaran alam sekitar. Perkembangan dalam sektor industri secara tidak langsung akan meningkatkan pembuangan sisa toksik sekali gus meningkatkan kandungan ion plumbum dalam sumber air. Penjerapan menggunakan karbon teraktif yang disintesis daripada biojisim dicadangkan kerana mudah, menjimatkan kos and mempunyai keupayaan untuk menyerap ion logam. Penyelidikan ini melaporkan karbon teraktif yang disintesis daripada bakau melalui pemanasan gelombang mikro dengan CO_2 untuk penyingkiran ion plumbum. Penghasilan karbon teraktif berasaskan bakau menggunakan pemanasan gelombang mikro dicadangan berikutan ketersediaan bakau di Malaysia dan pengurangan dalam masa pengaktifan dan penggunaan tenaga. Rangsangan permukaan (RSM) dilaksanakan untuk menentukan penyediaan optimum karbon teraktif daripada bakau iaitu pada 616W dan 6 minit. Kemudian, karbon teraktif yang telah optimum dianalisis menggunakan spektroskopi inframerah fourier transformasi (FTIR) dan penganalisis unsur. Melalui analisis FTIR, penjerapan Pb(II) ke karbon teraktif adalah disebabkan oleh regangan -OH. Analisis unsur menunjukkan karbon adalah unsur utama yang didapati dalam karbon teraktif Seterusnya, eksperimen dijalankan untuk menyiasat sifat penjerapan Pb(II) pada karbon teraktif berasaskan bakau. Penyingkiran tertinggi ialah 75.68%, direkodkan pada dos penjerap 0.4g dengan kepekatan 10 mg/L, pH 6 dan $30^{o}C$. Kajian isoterma dan kinetik penjerapan mengikuti model Langmuir dan pseudo tertib kedua. Parameter termodinamik mencadangkan sifat eksotermik dan spontan penjerapan Pb(II).

ACTIVATED CARBON FROM MANGROVE BY MICROWAVE IRRADIATION FOR ADSORPTION OF LEAD(II) IONS

ABSTRACT

Lead is a toxic heavy metal known as an environmental pollutant and the expansion of industries caused more effluents containing lead (II) ions are discharged to the water bodies. Adsorption approach was proposed using activated carbon derived from biomass due to ease in production, economical and ability to adsorb metal ions. The present research reports an activated carbon synthesized from mangrove via microwave heating in the presence of CO_2 to remove Pb(II) ions. The production of mangrove-based AC using microwave heating is proposed due to availability of mangrove in Malaysia and significant reduction in activation time and energy consumption. Response Surface Methodology (RSM) is implemented to determine the optimal variables in producing the activated carbon from mangrove at optimum conditions whereby the optimum conditions were achieved at 616W and 6 mins. The AC that had been optimized was characterized using an FTIR and an elemental analyzer. Through the FTIR analysis the adsorption of Pb(II) ions to AC was mainly due to -OH stretch. From the elemental analysis, carbon was the major element found in the prepared activated carbon. Batch experiments were performed to examine the adsorption behavior of Pb(II) on the mangrove-based activated carbon. The highest removal was 75.68% recorded at AC dose of 0.4g with concentration of 10 mg/L, pH 6 and 30^{o}C. The adsorption isotherm and kinetics studies showed that the adsorption followed Langmuir isotherm and PSO model respectively. The thermodynamic study suggested that the nature of the system was exothermic and spontaneous.

CHAPTER 1

INTRODUCTION

The first chapter present the overview of this study and the significance of adsorption via AC to remove Pb(II) ions. The sustainability aspects of the project are included at the end of the chapter.

1.1 Research Background

Heavy metals are metals and metalloids with large densities that are hazardous at ppb levels. Arsenic, cadmium, chromium, lead and zinc are some of the most prevalent harmful heavy metals found within the industrial effluent (Morifi et al., 2020). The contamination of heavy metal in waterbodies occurred close to industrial areas. According to Shahbudin and Kamal (2021), 55 rivers in Malaysia exceeded the cadmium limit, 44 rivers surpassed the iron limit, and 36 rivers exceeded the lead level. Due to the rapid expansion of industry, an increasing amount of harmful heavy metals infiltrated the river and land (Zhu et al., 2019). Heavy metals cause substantial harm to the water system as it cannot break down in addition to biological build-up and enrichment (Wang et al., 2020).

As highlighted above, lead is a toxic heavy metal known as an environmental pollutant. Lead is mainly used for the manufacturing of lead acid battery. The other uses of lead are rolled extrusions, lead pipes, pigments, cable sheathing and lead alloys. As a result of the expansion of these industries, more effluents containing lead (II) ions are discharged to the water bodies. The contamination of heavy metals in the water bodies imposed a hazardous effect on human health when they entered the food chain. Lead can have deleterious effects at very low concentrations on the central nervous and gastrointestinal system, as well defect the function of the kidney and liver. The World

Health Organization (WHO) has set a limit on the amount of lead in drinking water at 10 µg/L (Morifi et al., 2020). Hence, it is essential to eliminate lead from the wastewater.

1.2 Problem Statement

The expansion of industrial activities posed a significant danger to the environment particularly to water sources. Lead is a common heavy metal known as an environmental pollutant as it is typically present in the water sources. Effluent containing high level of lead (II) ions are discharged to the water bodies from various industries. Effluent from electrical, electroplating, mining and smelting industries has traces of lead (Alothman et al., 2019). In nature, they can be poisonous or carcinogenic, causing serious health issues for humans and aquatic ecosystems. Lead pollution in the environment may disrupt the resources by poisoning the water supply used for drinking and agriculture. Hence, lead removal from wastewater is a significant issue.

Biosorption, chemical precipitation, electrochemical treatment, ion exchange, membrane technology, photo-catalytic and solvent extraction are the approaches that are employed for wastewater treatment (Abas et al., 2015). However, the adsorption method is highly preferred to reduce the content of heavy metals in effluent before being discharged to the water bodies. Due to its economical and eco-friendliness, the adsorption process using AC is frequently utilised for heavy metal removal from wastewater (Renu et al., 2016). Aside from that, the activated carbons are favourable for high adsorption of heavy metal due to the high internal surface area and free valency (Angin and Sarikulce, 2017). Moreover, the activated carbon is flexible as it can be prepared from different organic substances. Mangrove bark from charcoal industries is made into adsorbent to adsorb heavy metals. These barks are cheap and plentiful, and they contain polyphenolic chemicals that are beneficial for metal ion adsorption at appropriate pH and temperature (Abas et al., 2015). Locally, mangrove is implemented in the construction of pilling of low-rise structures (Zakaria et al., 2021). The utilization of the waste generated from the pilling process can minimize disposal waste. Thus, activated carbon from mangrove is selected for the adsorption of Pb (II) ions.

1.3 Objectives

The aim of this research:

i. To perform characterization on the activated carbon derived from the mangrove

ii. To study the effect of initial concentration, solution temperature, AC dose and pH on the effectiveness of the prepared activated carbon

iii. To analyse the adsorption mechanism with the adsorption isotherm and kinetic models

iv. To investigate the adsorption behaviour from the thermodynamic parameters

1.4 Sustainability

The Sustainable Development Goals (SDGs) are goals to address the worldwide concerns. There are a total of 17 global goals and 3 of them closely related to the current research. The first one is Goal 6 which is clean water and sanitation. Low lead concentrations can contaminate the water bodies which also affect the source for drinking water. As highlighted in the previous section, less than 10mg/L lead content should be in the clean water. Consuming water with significant lead contained can damage the central nervous and gastrointestinal system. The rapid development in the industry contributed to the high lead content in the water bodies locally. Wastewater treatment plays a critical part in ensuring the effluent released to the water bodies are according to the specification. Adsorption via AC is an approach applied in treating the effluent to sustain clean water.

Next is Goal 12 that encourage environmentally sustainable production while also repurposing waste to minimize disposal. This research implemented mangrove as a precursor for the preparation of activated carbon. In Malaysia, mangrove is mangrove is implemented in the construction of pilling of low-rise structures and repurposing the waste generated from the construction activity minimizes disposal waste which corresponds to Goal 12. Lastly, Goal 14 that conserve the marine biodiversity. Our ocean's conservation needs to be a major priority as the health of people and its surrounding depends on it. This goal also relates to wastewater treatment. Effective wastewater treatment is crucial in protecting marine life as lead and its compounds can cause acute or chronic poisoning in organisms if they are present in significant levels in aquatic settings.

CHAPTER 2
LITERATURE REVIEW

The second chapter contains past findings and evaluations based on credible scientific records and references linked to this project. This chapter also provides an overview of activated carbon preparation and adsorption performance.

2.1 Adsorption of heavy metals

Heavy metals ion contamination in water bodies pose a threat to the modern world because these ions are poisonous and carcinogenic in nature. At small traces, heavy metal ions present in the water can affect the health and environment (Costa et al., 2020). Lead is the most prevalent and one of the most dangerous heavy metal contaminants, entering water sources because of numerous industrial processes. Redmon et al. (2020) highlights that lead's ability to easily assimilate into the human bodies gained the attention of fellow researchers. According to the database from the Environmental Protection Agency (EPA) and the World Health Organization (WHO) the limit contaminant of lead in clean water is 150 µg/L and 10 mg/L respectively. Numerous technologies are available and commercialized to treat wastewater from heavy metals and other contaminants. Chemical precipitation, coagulation, ion exchange, membrane separation and reverse osmosis are some of the conventional methods to remove heavy metals ions. These conventional methods of heavy metals removal have become less appealing due to its major drawback of low removal efficiency and high operational cost (Chakraborty et al., 2020). **Table 2.1** illustrates the benefits and drawbacks of some of the conventional techniques outlined by Al-Qodah et al. (2017) and Chakraborty et al. (2020).

In contrast, the adsorption technique has gained interest in heavy metal removal as it requires less energy utilization, simplicity of use and high removal (Tamjidi et al. 2019). Mass transfer is the chemical engineering fundamental associated with adsorption. Adsorption involves sorption of gases or liquids on a solid surface. The unbalanced forces on the solid surface will cause the molecules or atoms to remain on the solid surface upon collision. Physical and chemical adsorption are the two types of adsorptions. The interaction of intermolecular interactions, such as Van der Waals forces is categorized as physical adsorption. Physical adsorption is often performed at a low temperature, with a high adsorption rate, low adsorption heat, and is not selective. The weak intermolecular attraction does not alter the structure of the adsorbate molecules. Hence, the adsorbate is easily separated due to low adsorption energy. When it comes to chemical adsorption, links between molecules are formed and broken, which resulted from adsorption being induced by the action of chemical bonds. . The heat released for chemical adsorption is larger compared to physical adsorption as it requires higher activation energy. Additional details on the physical adsorption and chemical adsorption are listed out in **Table 2.2**. Physical adsorption and chemical adsorption are not mutually exclusive and typically occur simultaneously. In terms of wastewater treatment, there are many processes involved.

2.2 Activated carbon

AC are extensively employed in the field of adsorption, particularly as an adsorbent material in wastewater treatment. Activated carbon is derived from carbonaceous raw material that contains a considerable quantity of porous structure generated on it. Majority of the volatile non-carbon elements and a small proportion of the original carbon content are removed by thermal or chemical means, resulting in a porous structure with a large surface area. The manufacturing of cost-effective and beneficial activated carbon from organic or agriculture waste has become a large-scale effort as commercial activated carbons are usually expensive, owing to the substantial usage of expensive precursors. An example of commercial activated carbon is developed from coal. Aside from the low cost of organic or agriculture by-products, converting waste materials into AC, which is subsequently used to manage pollutants, is a highly fascinating notion from the standpoint of the environment and sustainability (Sajjadi et al., 2019). The efficiency of AC in adsorbing a spectrum of pollutants in liquids or gases has increase the utilization of activated carbon as an adsorbent (Koehlert, 2017). **Table 2.3** displays the generation of AC from various biomass.

2.3 Activation method of biomass-derived activated carbon

The activated carbon is prepared by a two-step process which begins with the carbonization step and is followed by an activation or modification step (Sajjadi et al., 2019). The initial stage is to increase the carbon content and develop initial porosity whereas the next stage helps to change the chemical and physical properties of the precursor, which further increases the sample porosity and performance which enhance the AC versatility (Baytar et. al, 2018). The precursor is heated to a relatively high temperature (between 400 and 600 °C), which causes carbonization, a thermal breakdown process that takes place in the absence of oxygen, to transform it into char (Lam et al., 2016). As for the activation stage, it can be performed either using physical activation or chemical activation. The latter allows the carbonized sample to impregnate either with H_3PO_4, $ZnCl_2$, KOH, or NaOH activating agent. Upon activating at high temperatures, the sample begins to form more porous structures. Due to the dehydrogenation capacity of the activation material, which limits the creation of volatile compounds during the activation process, chemical activation procedures permit for improved efficiency in the manufacture of activated carbon (Baytar et. al, 2018). Apart from the conventional activating agent, a researcher also uses sulfuric acid for the activation step for lead adsorption. Meanwhile, the other activation method allows CO_2 the continuously flow to activate the AC.

Table 2.1 Benefits and drawbacks of different heavy metal removal techniques

Method	Benefits	Drawbacks
Chemical precipitation	• Simple to use and cheap • Metals easily removed	• Sludge disposal issues due to large amount of sludge • Excessive chemical usage is required
Coagulation	• Dewatering and settling of sludge are facilitated • Appropriate for large-scale wastewater treatment	• Expensive due to high chemical consumption quantities • Large amounts of sludge are produced, and cause disposal problems
Ion-Exchange	• Selective for metal ions • High metal ions removal	• Expensive, and it cannot be employed on a large scale
Membrane filtration	• Less chemicals are utilized • Less sludge generation • Excellent separation selectivity • Low operating pressure • Minimal space is required	• High operating and maintenance costs
Reverse Osmosis	• High removal efficiency	• High energy consumption

Recent studies by Ahmad et al. (2021) and Yusop et al. (2021) uses microwave irradiation along with chemical activation for sample preparation. This is a form of a

Table 2.2 Differences between physical adsorption and chemical adsorption

	Physical adsorption	Chemical adsorption
Adsorption force	Van der Waals forces	Chemical bond forces
Adsorption heat	Small	Large
Adsorption layer	Single or multiple layers	Single layers
Adsorption rate	Rapid	Slow
Stability	Instable	Stable
Selectivity	Nonselective	Selective

physiochemical activation in which physical and chemical activation are combined. The char is impregnated with a chemical activating agent before being gasified by oxidizing gas at a relatively high temperature. The physicochemical activation step using a conventional furnace has many downsides such as high energy requirement and long activation period making this process not efficient. Thus, microwave irradiation has become a possible alternative by researchers since it requires shorter activation time and can significantly reduce theth amount of oxidizing gas used. Microwave energy causes dipole rotation at a rate of nearly a million times per minute in the atomic scale of the material. As a result of the frictional force between atoms and molecules within the sample, heat is produced and distributed quickly throughout the material (Lam et al., 2016). Besides, the microwave irradiation technique provides selecting heating and can control side reactions, decreasing the reaction time. Hence, consuming fewer power than conventional heating leads to low production cost and contributes to green synthesis of activated carbon (Shao et al., 2019).

Table 2.3 Sources of biomass and its application

Biomass	Application	Reference
Apricot stone	Removal of Pb^{2+} and $Cu2^{+}$ ions	Abbas, 2021
Empty fruit bunch	Removal of Pb^{2+} ions	Elias et al., 2021
Kenaf core	Removal of Pb^{2+}, Cu^{2+} ions and Congo Red dye	Mandal et al., 2021
Date pits	Removal of Pb^{2+} ions	Krishnamoorthy et al., 2019
Juniperus Procera leaves	Removal of Pb^{2+} and Cr $^{6+}$ ions	Ali et al., 2019
Pistachio wood	Removal of Pb^{2+} ions	Sajjadi et al., 2019

A study was conducted by Foo and Hameed (2012), to determine the effective microwave power and radiation time for the synthesis of the activated carbon via the microwave heating method. Increasing the microwave power from 180W to 600 W observed an increasing in adsorption uptake and beyond 600 W the adsorption uptake begins to decrease. The plausible reason behind this is the expansion of the carbon structure at higher heating power and further increasing the microwave power reduces the surface area and porosity of the AC. As for the radiation time, maximum adsorption uptake was recorded at 6 min when the radiation time is manipulated from 4 to 8 min. Initially, the adsorption uptake increased with time and then began to decrease at 7 min. Extending the exposure duration increases reaction rates, but it will eventually degrade the pore structure of the activated carbon.

2.4 Characterization of activated carbon

The reported works on activated carbon conducted a characterization study to know the activated carbon surface morphology and adsorbing tendency nature. Scanning electron microscope (SEM) characterization images are useful in studying the pore size and structure. The activated carbon derived from biomass showed more pores on the surface which explains the increase in adsorption efficiency. Fourier Transform-Infrared (FTIR) Spectroscopy is used in the characterization of prepared activated carbon to analyse the surface functional groups. The porosity of activated carbon as well as the chemical reactivity of functional groups at the surface influence its adsorption capacity. From the FTIR, different functional groups are identified which contributes to the binding of different molecular species onto the adsorbent's surface (Omri and Batis, 2013). Some works use elemental analyzers for elemental analysis. The objective of using the equipment is to determine the composition of elements in the AC. For instance, the precursor from acacia wood has relatively high fixed carbon of 24.75% which explains the high adsorption capacity (Yusop et al., 2021)

2.5 Parameters affecting the adsorption capacity

The biomass listed in **Table 2.3** was studied on their adsorption capacity in which the removal of lead ions is the common heavy metal chosen by the researchers. The pH of the solution influences the adsorption process and removal percentage. The removal percentage increases until it reaches the optimum pH and then decreases. The studies show high adsorption capacity in the pH range of 4 to 6 which indicates that the removal of lead ions work best in acidic conditions. Beyond the acidic range, the adsorption capacity starts to decrease. The activated carbon from Juniperus Procera leaves shows the highest removal percentage of 97% recorded at pH 4.6. The declination of the adsorption capacity at higher pH range (pH > 6) is due to the formation of hydroxyl complexes and at lower pH (pH < 4) the removal of Pb(II) ions is hindered by the H^+ and Pb^{2+} competing for the same active sites on the adsorbent surface reported by Ali et al. (2019).

The adsorption efficiency also depends on the initial concentration of the adsorbate solution. However, this factor is not studied for all the biomass listed in **Table 2.3**. Kenaf core, Juniperus Procera leaves and Pistachio wood are the biomass that are used to study for the initial concentration of solution whereby the concentration of lead ions is manipulated. The results reported are consistent as the lead ions removal percentage drops at high initial concentration of lead ions. Despite the strong affinity between the activated carbon surface and Pb^{2+} ions, availability of adsorption sites on the adsorbent surface is limited (Sajjadi et al., 2019). Hence, causing the decreasing removal efficiency at higher concentrations.

It is also critical to investigate the adsorption behavior as it relates to temperature. The thermodynamics parameters are useful in determining the adsorption behavior at different solution temperature. The study on solution temperature is conducted by some researchers as there is the need to acquire the thermodynamic parameters. The researchers claimed that the lead ions removal percentage increases with solution temperatures. The optimum solution temperature are different as different researchers use different maximum solution temperature. The optimum solution temperatures are in the range of 40°C to 60°C. Mandal et al. (2021) suggested that increasing the temperature will also increase the interparticle diffusion rate in the pores.

The adsorbent dose is an essential parameter since it defines the capacity of an adsorbent for a given initial concentration. The adsorption effectiveness for lead ions as a function of adsorbent dosage is examined by Elias et al. (2021) and Krishnamoorthy et al. (2019). The researchers who conducted the study on the effect of adsorbent dosage for lead removal agreed that the increase in adsorbent dose also increased the rate of lead ions removal. The presence of more adsorption sites and more adsorbent for the same quantity of adsorbate might be the cause for the improvement in efficiency. However, further increasing the adsorbent dose did not result in increased Pb (II) absorption. This concludes that the optimal adsorbent to adsorbate dose ratio has been achieved, and all active sites on the adsorbent dosage have been occupied.

2.6 Adsorption Mechanism

2.6.1 Adsorption Isotherm

Adsorption isotherm models are commonly used to assess adsorbent performance for certain adsorbate ions. The two most isotherm models applied by the researchers to study the interaction between the lead ions and activated carbon are the Langmuir model and Freundlich model. Langmuir model is represented by Eq. (2.1) and the following are the main assumptions of the model:

i. Adsorption occurs at the particular binding sites on the adsorbent surface.
ii. The adsorption sites on the adsorbent's surface are all alike.
iii. A monolayer of adsorbed molecules covers the surface of the adsorbent.
iv. The adsorbed molecules on the adsorbent surface do not interact with one other.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{2.1}$$

where,

C_e: Concentration of adsorbate solution at equilibrium (mg/L)

K_L: Langmuir constant

Q_m: Maximum adsorption capacity (mg/g)

q_e: Adsorption capacity at equilibrium (mg/g)

The Freundlich isotherm model depicts the adsorption of molecules on the adsorbent surface in multilayers and heterogeneously. Freundlich isotherm implies reversible adsorption on heterogeneous surfaces and predicts a rise in concentration on the adsorbent surface as adsorbate ion concentration increases. (Araújo et al., 2018). The equation of the model is demonstrated with Eq. (2.2). Ahmad et al. (2021) stated that the adsorption capacity increases with increasing K_F value. Surface heterogeneity is shown by the factor $1/n_F$. The n value should be between 1 and 10 for good adsorption (Faheem et al., 2018).

$$q_e = K_F C_e^{1/n_F} \tag{2.2}$$

where,

C_e: Concentration of adsorbate solution at equilibrium (mg/L)

q_e: Adsorption capacity at equilibrium (mg/g)

K_F: Freundlich constant

$1/n_F$: Freundlich heterogeneity factor

2.6.2 Adsorption Kinetics

During the adsorption of a substance to the surface of the adsorbent, there are three primary processes. The first stage involves the molecular mass transfer from the solution to the adsorbent surface. Internal molecular diffusion then occurs to the adsorption sites on the adsorbent. The adsorption achieved completion upon reaching the final stage (Kecili and Hussain, 2018). It is critical to investigate adsorption kinetics to determine the adsorption mechanism. Adsorption kinetics models such as the pseudo first order and pseudo second order models are commonly used in adsorption systems for this purpose. The adsorption will follow the pseudo first order model if there is a simple particle diffusion involved in a two-step adsorption mechanism mentioned by El-Banna et al. (2018). If the adsorption data fit the pseudo second order it indicates chemisorption is the rate limiting step. Chemisorption is the process of exchanging electrons between the adsorbent active sites and the adsorbate. Chemisorption, on the other hand, creates just one layer of molecules on the surface before attaching to other layers of physically adsorbed molecules (Saeidi et al., 2015). Eq. (2.3) represent the pseudo 1st order and following are the main assumptions of the model:

i. Adsorption takes place at the specific binding sites on the adsorbent surface
ii. The formation of a layer on the adsorbent surface does not correlate with the adsorption energy.
iii. The rate of adsorption is governed by the first-order equation.
iv. The adsorbed molecules on the adsorbent surface do not interact with one other.

$$q_t = q_e[1 - exp(-k_1 t)] \tag{2.3}$$

where,

k_1: Rate constant of pseudo 1st order

q_e: Adsorption capacity at equilibrium (mg/g)

q_t: Adsorption capacity at time, t (mg/g)

The assumptions are also applicable to pseudo second order. The sole difference between the pseudo first order and pseudo second order kinetic models is the rate of the model and is demonstrated by Eq. (2.4).

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{2.4}$$

where,

k_2: Rate constant of pseudo 2nd order

q_e: Adsorption capacity at equilibrium (mg/g)

q_t: Adsorption capacity at time, t (mg/g)

2.6.3 Thermodynamics

Thermodynamic studies are useful in predicting adsorption behaviour under temperature impact. The Gibbs energy, enthalpy and entropy are the thermodynamic parameters that store the fundamental information about the nature of an adsorption system (Ahmad et al., 2021). The Gibbs Energy may be used to measure the spontaneity of the adsorption process, ΔG^o . When ΔG^o is in the range of -20 to 0 kJ/mol indicates a physisorption process whereas values between -400 to 80 kJ/mol implies a chemisorption process (Pearlin et al., 2014). The negative and positive value of the enthalpy indicates the process is exothermic and endothermic respectively. From the entropy, the randomness of the adsorption process can be established. Eq. (2.5) is the Van’t Hoff equation applied to compute the standard enthalpy and entropy. The Gibbs energy is given by Eq. (2.6).

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{2.5}$$

$$\Delta G^o = -RT \, ln \, K_c \tag{2.6}$$

where,

K_c: Equilibrium constant

R: Gas constant (kJ/mol.K)

ΔG^o: Gibbs energy (kJ/mol)

ΔH^o: Enthalpy change (kJ/mol)

ΔS^o: Entropy change (kJ/mol.K)

CHAPTER 3
METHODOLOGY

This chapter discloses the overall experimental aspects of the project. This project is structured to realize the objective of the research. It includes the overall structure of the project, activated carbon optimization with software Design Expert Central Composite Design (CCD), materials and equipment and lead (II) ions adsorption experiment.

3.1 Research Methodology

Figure 3.1 reveals the overall structure of the project. The activated carbon will be prepared with a two-stage process whereby the first stage is the carbonization stage and followed by the activation stage. Mangrove wood is cut into small pieces and let it dry in the oven for 1 week at a temperature of 100^{o}C to remove the moisture content. The dried mangrove wood will be crushed into 250µm mesh size and store in a zip bag Approximately 7.5 g of the fine mangrove powder was inserted into the quartz and closed the top with a cork with two tubes which allows CO_2 gas to flow into it and oxygen and other volatile components to exit the other. The quartz will be placed in a modified microwave where the microwave power and radiation time can be adjusted. The setup of the microwave irradiation is represented by **Figure 3.2**. Tube A allows the CO_2 source to enter the system and oxygen and other volatile components will exit through Tube B.

3.2 Materials and Equipment

Specified materials and equipment are needed to conduct the project. **Table 3.1** depicts the equipment that are required for the experiment. The materials used in the experiment are listed out in **Table 3.2**.

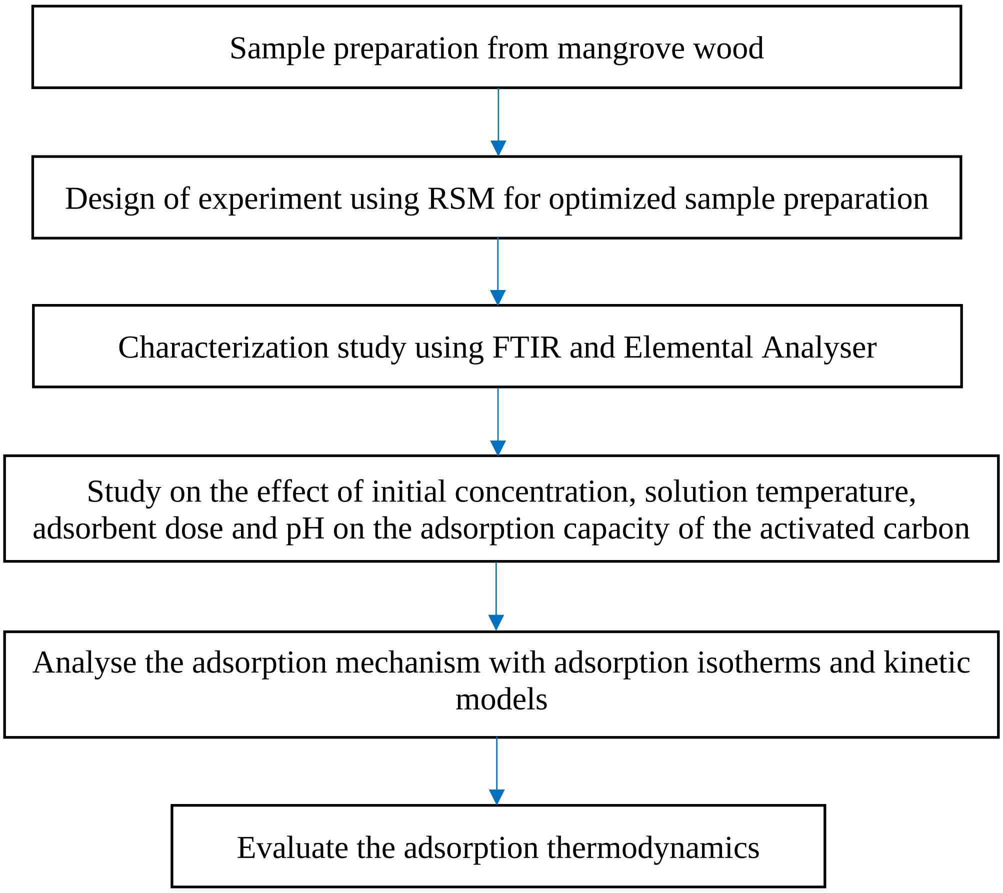

Figure 3.1 Overall structure of the project

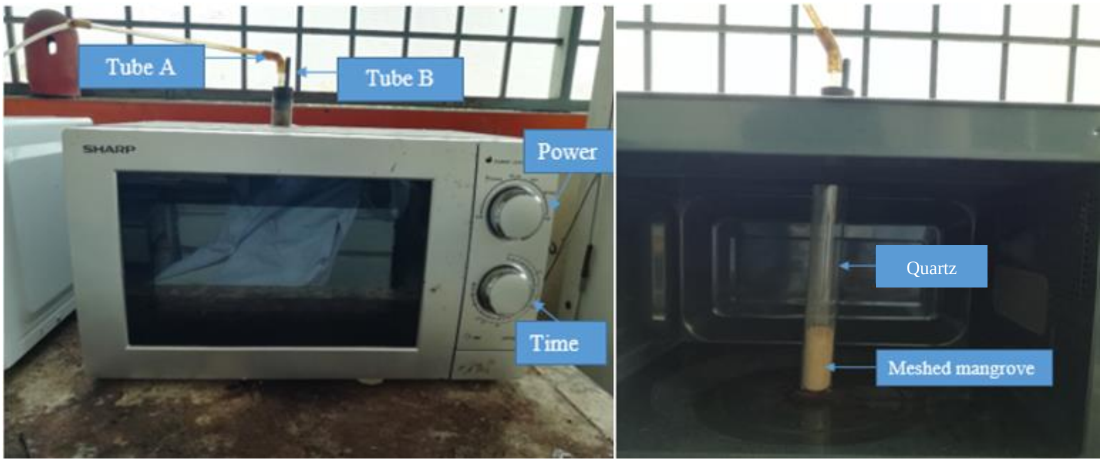

Figure 3.2 Setup of modified microwave irradiation

Table 3.1 List of equipment

Equipment	Purpose
Grinder	Crushing of mangrove
Microwave oven	Activation step
Shaking waterbath	Isothermal adsorption
Fourier Transform-Infrared (FTIR) Spectroscopy	Determine functional groups present on the sample
CHNS Elemental Analyzer	Identify the composition of the sample
UV-Vis Spectrophotometric	Determine the final concentration of solution

3.3 Adsorbate solution preparation

1.5991g of $Pb(NO_3)_2$ is dissolved in 1000ml of deionized water to prepare a stock solution containing 1000mg/L of Pb(II) ions. Different concentrations (10 to 50 mg/L) are prepared using serial dilution. Eq. (3.1) can be applied to dilute the solution.

$$M_1V_1 = M_2V_2 \tag{3.1}$$

where,

M_1: Concentration of stock solution (mg/L)

M_2: Concentration of adsorbate solution (mg/L)

V_1: Volume of stock solution (L)

V_2: Volume of adsorbate solution (L)

Table 3.2 List of materials

Materials	Purpose
Deionized water	Dilution of solution
Mangrove	Raw material of synthesizing activated carbon
NaOH pellets	Preparation of 0.1 M NaOH
$Pb(NO_3)_2$ pellets	Preparation of Pb(II) stock solution
37% HCl stock solution	Preparation of 0.1 M HCl

3.4 Design of experiment

Design Expert 13.0 by Stat-Ease, Inc was utilized for the optimization of mangrove-based activated carbon. Microwave power and time are the variables that will be manipulated to achieve activated carbon at optimum conditions. The microwave power was manipulated from 364W to 616W whereas the activating time was varied from 2min to 6min. The main response will be the percentage removal of lead ions from the adsorbate solution and AC yield. Response Surface Methodology was applied because it can easily get the optimum value and complete analysis via ANOVA. The low and high levels of each factor to be studied were shown in **Table 3.3**. with the responses for the study which is the Pb(II) removal percentage (%) and the yield (%). High values are denoted by +1 whereas, low values are denoted by -1. The information was added into the Design Expert Central Composite Design (CCD) to generate the experimental design matrix required. Based on the Design Expert Central Composite Design, a total amount of 13 run simulations required in this study. **Table 3.4** illustrates the experimental design matrix generated in Design Expert.

Table 3.3 Experimental variables and code values

		Unit	Notation	Coded values		
				-1	0	+1
Preparation Variables	Radiation Power	Watt (W)	X_1	364.00	511.00	616.00
	Radiation Time	Minutes (min)	X_2	2.00	4.00	6.00
Responses	Pb(II) ions removal	%	Y_1	-		
	Mangrove-based activated carbon's yield	%	Y_2	-		

3.5 Characterization studies

The characteristics of the optimized AC was determined using FTIR and CHNS Elemental Analyzer. Once the optimized activated carbon was prepared, 0.2 g of the AC was seal in a zip bag. Then, another 0.2 g of the activated carbon was added to 10 mg/L Pb(II) solution at pH 6 and leave it for 24 hours in a shaking water bath maintained at 30^{o}C for adsorption. After 24 hours, the activated carbon was collected and dried and put in a zip bag. These two samples are sent to the Chemistry Laboratory for FTIR analysis. FTIR analysis was done for sample before and after adsorption. One sample of 0.2 g was sent to the Analytical Laboratory for elemental analysis.

3.6 Batch equilibrium studies

The influence of the solution initial concentration, pH, solution temperature and adsorbent dosage will be studied for the Pb(II) ion removal and adsorption capacity of

Table 3.4 Experimental design matrix generated by Design Expert

Std	Run	Factor 1: Radiation Power (W)	Factor 2: Radiation Time (min)
2	1	364	2
12	2	354	6
7	3	511	4
10	4	616	2
11	5	511	6
9	6	511	6
13	7	616	4
3	8	616	6
5	9	511	6
6	10	616	6
8	11	616	4
4	12	616	6
1	13	364	6

the prepared activated carbon. The first parameter is initial concentration. The solution initial concentration will be increased from 10 to 50 mg/L while maintaining the temperature at 30^{o}C and pH 6 with an adsorbent dosage of 0.2g. Then, the experiment was repeated at 45^{o}C and 60^{o}C. For the third parameter, the adsorbent dosage is varied from 0.1 to 0.5g for 10 mg/L Pb(II) concentration while maintaining the pH and temperature at 6 and 30^{o}C respectively. Finally, the pH is manipulated from 2 to 8 while the other parameters are remained constant. The pH was altered by adding drops of 0.1M HCl and 0.1M NaOH. The data obtain from the study will be used to:

i. Calculate the amount of removal at time, t and at equilibrium

$$q_t = \frac{(C_o - C_t)V}{W} \tag{3.2}$$

$$q_e = \frac{(C_o - C_e)V}{W} \tag{3.3}$$

ii. Calculate the removal percentage of lead ions

$$\%R = \frac{(C_o - C_e)}{C_o} \tag{3.4}$$

where,

C_e: Concentration of adsorbate solution at equilibrium (mg/L)

C_o: Initial concentration of adsorbate solution (mg/L)

C_t: Concentration of adsorbate solution at time, t (mg/L)

q_e: Adsorption capacity at equilibrium (mg/g)

q_t: Adsorption capacity at time, t (mg/g)

V: Volume of solution (L)

W: Weight of adsorbent (g)

%R: Removal percentage of lead ions (%)

The summary of the parameters for the batch adsorption study with their specified range used in the project is tabulated in **Table 3.5**. The result from the batch adsorption study used for determining the adsorption mechanism and thermodynamics.

Table 3.5 Summary of parameters and their respective range

Parameters	Range	Reference
Initial concentrations (mg/L)	10, 20, 30, 40, 50	Chi et al., 2017
Temperature (^oC)	30, 45, 60	Ahmad et al., 2021
Adsorbent dosage (g)	0.1, 0.2, 0.3, 0.4, 0.5	Ali et al., 2019
pH	2, 4, 6, 8	Zhang et al., 2021