# REMOVAL OF ZINC (II) IONS FROM INDUSTRIAL WASTEWATER BY ACTIVATED CARBON SYNTHESIZED FROM MANGROVE *(RHIZOPHORA MANGLE)*

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**by**

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Nanthini Mohana Suntharam

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## TABLE OF CONTENTS

**LIST OF FIGURES**

## LIST OF TABLES

# LIST OF SYMBOLS

| Symbol | Description | Unit |
|---|---|---|
| $\frac{1}{n}$ | Heterogeneity factor | - |
| A | Arrhenius factor | - |
| $C_e$ | Equilibrium metal ion concentration after adsorption | M or ppm |
| $C_f$ | Final concentration of metal ion | M or ppm |
| $C_0$ | Initial concentration of metal ion | M or ppm |
| Ea | Activation energy | kJ/mol |
| $k_1$ | Rate constant for PFO kinetic model | $min^{-1}$ |
| $k_2$ | Rate constant for PSO kinetic model | g/mg.min |
| $K_F$ | Freundlich rate constant | L/mg |
| $K_L$ | Langmuir rate constant | L/mg |
| M | Amount of adsorbent | g |
| $M_1$ | Concentration of stock solution | M or ppm |
| $M_2$ | Final concentration of solution after dilution | M or ppm |
| $q_e$ | Adsorption uptake at equilibrium | mg/g |
| $q_{max}$ | Maximum adsorption capacity | mg/g |
| $q_t$ | Adsorption capacity at time t | mg/g |
| R | Gas constant | J/mol.K |
| T | Absolute temperature | K |
| t | Time | Min |
| V | Volume of Zn (II) solution | ml |
| $V_1$ | Volume of stock solution required | ml |
| $V_2$ | Final volume of diluted solution | ml |

| | | |
|---|---|---|
| $W$ | Watt (unit of power) | - |
| $W_o$ | Initial weight of char | g |
| $W_f$ | Final weight of char | g |
| $W_{char}$ | Weight of char | g |
| $W_{KOH}$ | Weight of KOH | g |
| $\Delta G°$ | Standard Gibbs free energy | J/mol |
| $\Delta H°$ | Standard enthalpy | J/mol |
| $\Delta S°$ | Standard entropy | J/mol |

**Greek letter**

| | |
|---|---|
| $\sigma$ | Standard deviation |

# LIST OF ABBREVIATION

| Symbol | Description |
|---|---|
| AC | Activated Carbon |
| ATR | Attenuated Total Reflectance |
| C | Carbon |
| CAC | Commercially Activated Carbon |
| CCD | Central Composite Design |
| CHNS | Carbon Hydrogen Nitrogen Sulphur |
| Co | Cobalt |
| CO | Carbon Monoxide |
| $CO_2$ | Carbon Dioxide |
| DTGS | Deuterated Triglycine Sulphate Detector |
| Eu | Europium |
| Fe | Iron |
| FTIR | Fourier Transform Infrared |
| HCL | Hydrochloric Acid |
| $HNO_3$ | Nitric Acid |
| $H_2$ | Hydrogen |
| $H_2O$ | Water |
| $H_2SO_4$ | Sulfuric Acid |
| $H_3PO_4$ | Phosphoric Acid |
| IR | Impregnation Ratio |
| K | Potassium |
| $K_2CO_3$ | Potassium Carbonate |

| | |
|---|---|
| KOH | Potassium Hydroxide |
| KOH-AC | KOH Activated Carbon |
| Mn | Manganese |
| MW | Molecular Weight |
| $N_2$ | Nitrogen |
| Na | Sodium |
| NF | Nanofiltration |
| NaOH | Sodium Hydroxide |
| PFO | Pseudo First Order |
| Pb | Lead |
| PSO | Pseudo Second Order |
| $R^2$ | Correlation Coefficient |
| RO | Reverse Osmosis |
| RSM | Response Surface Methodology |
| SEM | Scanning Electron Microscope |
| SDG | Sustainability Development Goals |
| UF | Ultrafiltration |
| UV-VIS | Ultraviolet Visible Spectrophotometer |
| Zn | Zinc |
| $ZnCl_2$ | Zinc Chloride |

**PENYINGKIRAN ION ZINK (II) DARI AIR SISA INDUSTRI DENGAN KARBON TERAKTIF DIPERBUAT DARIPADA BATANG BAKAU *(RHIZOPHORA MANGLE)***


## ABSTRAK

Pencemaran air adalah salah satu isu utama di Malaysia, disebabkan oleh pembebasan air sisa industri yang mengandungi logam berat. Bahan penjerap yang sesuai diperlukan untuk mengatasi masalah ini. Karbon teraktif adalah salah satu penjerap yang biasa digunakan untuk proses penjerapan. Karbon teraktif yang tersedia secara komersial (CAC) adalah mahal kerana ia diperbuat daripada sumber yang tidak boleh diperbaharui dan memerlukan kaedah pemprosesan lanjutan untuk dihasilkan. Dalam beberapa tahun kebelakangan ini, pengeluaran untuk karbon teraktif daripada produk pertanian telah mendapat perhatian kerana keupayaannya dalam meningkatkan proses penjerapan. Oleh itu, kajian ini memfokuskan kepada potensi penggunaan sisa pertanian yang banyak terdapat di Malaysia iaitu kayu bakau, sebagai pelopor kepada penyediaan bahan penjerap kos rendah yang boleh digunakan untuk penyingkiran ion Zn (II) daripada air kumbahan industri. Penyediaan karbon teraktif melalui pemanasan gelombang mikro dibuat pada kuasa dan jangka sinaran yang berbeza. Pengoptimuman kuasa dan masa sinaran gelombang mikro telah dilakukan menggunakan *Response Surface Methodology (RSM).* Karbon teraktif yang optimum dihasilkan pada 616 W dan 4 minit di bawah pengaktifan fizikal dengan menggunakan gas $CO_2$. Selain itu, proses penjerapan menggunakan karbon teraktif berasaskan bakau disiasat dalam pelbagai keadaan. Penjerapan ion Zn (II) telah dijalankan dalam proses kelompok. Daripada data eksperimen, nisbah impregnasi KOH yang ideal adalah pada 0.5 dengan 98.97% hasil karbon teraktif dan penyingkiran ion zink (II) sebanyak 84.44%. Sifat permukaan dan morfologi dan kumpulan berfungsi penjerap yang disediakan telah diperiksa. Fasa keseimbangan semasa penjerapan untuk semua eksperimen dicapai dalam masa 5 jam. Kepekatan awal larutan Zn (II) dikaji pada kepekatan yang berbeza seperti 10, 20, 30, 40 dan 50 ppm. Manakala suhu yang berbeza dipilih untuk eksperimen ialah 20, 40 dan 60°C. Penyingkiran ion Zn (II) dan kapasiti penjerapan tertinggi dicapai pada 10 ppm dan 60°C dengan peratusan masing-masing iaitu 82.70% dan 20.4043 mg/g. Model isoterma Langmuir mempamerkan kesesuaian terbaik untuk proses penjerapan. Kapasiti penjerapan maksimum dengan menggunakan isoterma Langmuir ialah 27.6243 mg/g. Data ini juga ini sesuai dengan kinetik *pseudo-second order* dengan nilai $R^2$ iaitu 0.9999. Akhirnya, kajian termodinamik membuktikan bahawa proses penjerapan adalah endotermik. Proses ini berlaku secara spontan dan lebih cepat pada suhu yang tertinggi iaitu 60°C.

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## ABSTRACT

Water pollution has become one of the major issues in Malaysia, due to the release of industrial wastewater containing heavy metals. A suitable adsorbent is required to overcome this problem. Activated carbon is one the common adsorbent used for adsorption processes. Commercially available activated carbon (CAC) is expensive because it is made from non-renewable resources and require advanced processing methods to be produced. In recent years, production for activated carbon from agricultural products has gained attention for its ability in enhancing adsorption processes. Therefore, this study focuses on the potential use of agricultural wastes that are abundantly available in Malaysia, which is mangrove wood, as the precursor for the preparation of inexpensive adsorbent that can be applied to eliminate Zn (II) ions from industrial wastewater. The preparation conditions of the char through microwave heating were made at various radiation power and time. The optimization of microwave radiation power and time was performed using Response Surface Methodology (RSM). The optimal activated carbon was obtained at 616 W and 4 mins under physical activation with $CO_2$. Apart from that, the adsorption process using the mangrove-based activated carbon was investigated under several conditions. The adsorption of Zn (II) ions was performed in batch system. From the experimental data, the ideal KOH impregnation ratio was at 0.5 with 98.97% of activated carbon yield and zinc (II) ions removal of 84.44%. The surface properties and morphology and functional groups of the prepared adsorbents were examined using Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR) and CHNS Elemental Analyzer. The equilibrium phase during adsorption for all batch experiment was reached within 5 hours. The initial concentration of Zn (II) solutions was studied at different concentrations such as 10, 20, 30, 40 and 50 ppm. Whereas the varying temperatures selected for the experiment were 20, 40 and 60°C. The highest Zn (II) ions removal and adsorption capacity was reached at 10 ppm and 60°C with percentages of 82.70% and 20.4043 mg/g respectively. The Langmuir isotherm model exhibit the best fit for the adsorption carried out. The maximum adsorption capacity using Langmuir isotherm was 27.6243 mg/g. The experimental data was also well fitted with pseudo-second order kinetics with $R^2$ value of 0.9999. Finally, the thermodynamics study proved that the adsorption process is naturally endothermic. The process is spontaneous and faster at higher temperature of 60°C.

# CHAPTER 1: INTRODUCTION

## 1.1 Research Background

In the late centuries, water pollution became one of the universal problems that the society should notice and discuss about. Industrialization and globalization over the decades are the source of pollutant emissions especially heavy metals causing serious health problems in many countries. Heavy metals are categorized as metallic elements having a high relative density than water. Heavy metals are highly produced by service industry, refinery, leather industry, power industry, tannery industry and fertilizer industry. Heavy metals such as Chromium (Cr), Copper (Cu), Cadmium (Cd), Nickel (Ni), Arsenic (As), Lead (Pb) and Zinc (Zn) have high solubility in aquatic settings and can be taken up by living creatures when substantial amounts of metal-contaminated wastewater are discharged into the environment. These metals travel along the food chain and finally accumulate in the human body. High quantities of heavy metals in the human body can cause catastrophic disorders including damage to the nervous system, cancer, renal failures, and even death (Al-Saydeh et al., 2017). According to the Environmental Quality (Sewage and Industrial Effluents) Regulations, Environmental Quality Act 1974, there is certain limit for the discharge of heavy metals in Malaysia specifically for areas classified as Standard A and Standard B (Zwain et al., 2014).

The 23$^{rd}$ most prevalent naturally forming element in the Earth's crust is zinc but it's concentration in the wastewater is increasing unnaturally due to industrial activities such as galvanizing processes, manufacturing of paints, rubber, plastics, batteries, textiles, and electrical equipment, mining and mineral processing, fossil fuel combustion and landfill spills. Although humans can tolerate huge amounts of zinc, excessive exposure can result in serious health issues like stomach cramps, vomiting, skin irritations, anaemia, and nausea (Zwain et al., 2014). Therefore, metals like zinc need to be removed from industrial wastewater. Several methods were introduced prior to the removal of zinc from industrial wastewater such as chemical precipitation, hydroxide precipitation (Huisman et al., 2006), sulphide precipitation (Özverdi & Erdem, 2006), chelating precipitation (Matlock et al., 2002), ion exchange (Alyüz & Veli, 2009), adsorption (Dias et al., 2007; Kang et al., 2008) membrane filtration, coagulation and flocculation, flotation and electrochemical treatment (Fu & Wang, 2011). Of all these methods, adsorption is preferred for its high removal efficiency of heavy metals even at low wastewater concentrations, lesser generation of sludge, user-friendly and high versatility.

Adsorption method is utilized effectively in the industry for effective purification and separation technique for wastewater treatments by using commercial activated carbon (CAC). According to Fu and Wang in 2011, adsorption, which is a relatively new and developing process, is the most efficient form of removal technique when compared to other methods since it allows for design flexibility, produces high-quality treated effluent, and is reversible (Fu & Wang, 2011). The adsorbents employed in the procedure can be renewed using an appropriate desorption technique due to their reversibility. There are various characteristics that should be addressed while treating industrial wastewater for the elimination of heavy metals. This comprises adsorbent and adsorbate physical and chemical characteristics, temperature, contact duration, pH, and adsorbate concentration in liquid.

However, CAC remains as an expensive material and therefore activated carbon can be prepared using natural materials and agricultural wastes (Kazemipour et al., 2008). Recently, adsorption by agricultural waste is used as an economical and a realistic method for removing various impurities from aqueous solutions. Many studies were conducted using different types of activated carbons made from Mucuna pruriens seed shells (Igwegbe et al., 2016), sawdust, rice hull, wheat straw, sugarcane bagasse (Osman et al., 2010), chitosan (Babel & Agustiono Kurniawan, 2003) and mangrove (Zulkarnain et al., 1993). Among these, mangrove can make a good raw material for low-cost carbon precursor to be synthesized as activated carbon. This is because mangrove is abundantly available in Malaysia and most of the parts of the tree contribute to producing activated carbon for the elimination of various heavy metals from industrial wastewater. Moreover, according to Zakaria et al. (2021), mangrove pile was used to obtain the highest yield of activated carbon compared to natural materials such as paulownia wood, olive stone and apricot shell (Zakaria et al., 2021).

The adsorption process is highly dependent on the characteristics of adsorbate and adsorbent surface. The activated carbon is produced by carbonization at high temperatures with an inert atmosphere after vacuum drying. Then, the activation is carried out which affects the characterization of activated carbon. The activation process leads to the formation of porous structure on the activated carbon. There are mainly two types of activation processes, namely, physical activation and chemical activation. In physical activation, which is also identified as thermal activation, the char is produced from carbonization of the raw material in an oxidizing environment that partially gasifies at elevated temperatures. The examples of oxidants that can be used are such as steam and $CO_2$. Whereas the precursor is impregnated with chemical reagents such as $H_3PO_4$, $ZnCl_2$, Na or K hydroxides or salts for chemical activation. After impregnation, the materials are carbonized with inert atmosphere and then are washed to remove chemical. After washing, the pores of the activated carbon will be available for adsorption (Prauchner & Rodríguez-Reinoso, 2012).

In this final year project, it is proposed to prepare mangrove-based activated carbon and study its removal efficiency of heavy metal which is zinc ($Zn^{2+}$) in industrial wastewater. Thepreparation and activation of activated carbon and activation conditions including adsorption isotherm by employing Langmuir and Freundlich isotherm models, adsorption kinetics and its performance are optimized prior to yielding of the activated carbon. Furthermore, the characterization of activated carbon such as elemental analysis, functional groups and surface morphology will be studied by using FT-IR analyzer, CHNS analyzer and scanning electron microscopy (SEM). The project is further continued by conducting a batch equilibrium study by varying several parameters like contact time, initial concentration of adsorbate, chemical impregnation ratio and the initial temperature of solution. Also, thermodynamics studies are performed to explore the effects of temperature of solutions on the nature of the adsorption process.

## 1.2 Problem Statement

Malaysia has been experiencing tremendous growth in the industrial sector for the past century, but the side effect of rapid industrialization should not be overlooked. Heavy metal pollution is a major problem due to industrialization in our country lately. One of the metals that is used widely in various industries is zinc. According to Environmental Quality Act 1974; Environmental Quality (Industrial Effluent) Regulations 2009, the permitted concentration of zinc in industrial effluent for Standard A and B is 2.0 mg/L. Accumulation of heavy metals like zinc is hazardous to the food chain. Therefore, it is important to treat wastewater discharged from industries before releasing into freshwater bodies in Malaysia. A significant majority of studies have been carried out using different metal removal technologies, namely, ion exchange, adsorption, precipitation coagulation and flocculation, electrochemical treatment, and membrane filtration. However, there are some limitations using these methods. For instance, precipitation causes large amount of sludge production while ion exchange and membrane filtration require higher operational costs (Kazemipour et al., 2008). Further significant drawbacks using these methods are high energy requirements and incomplete removal of metals (Barakat, 2011). Among all these methods, adsorption is a potent technology for treating both domestic and industrial wastewater. Nevertheless, the adsorption technology requires higher cost due to usage and regeneration of great amount of adsorbents which restricts its application. To make this technology feasible and eco-friendly, studies on the elimination of zinc have shifted their attention to naturally occurring materials, which are also widely accessible. The suitable low-cost adsorbent utilized for the elimination of heavy metals from the industrial wastewater is activated carbon because the disposal is relatively easier, safer and the cost can be minimized. Low-cost adsorbents are adsorbents that require a little bit of preparation, readily available or is a waste product of industries. Activated carbon are effective because they have high surface area, good porosity, and well-developed pore distribution (Paryanto et al., 2019). Thus, it is crucial to discover a low-cost alternative raw material and preparation technique to synthesize suitable activated carbon for the elimination of zinc from industrial wastewater. In this study, the low-cost raw material chosen is the mangrove wood which is abundantly available in Malaysia. The effectiveness of the adsorbents to adsorb the zinc (II) ions is studied. Accordingly, the surface characteristics which makes the adsorbent to be suitable for adsorption are investigated.

## 1.3 Research Objectives

The objectives of the research are:

i. To study the physical and chemical properties of activated carbon such as surface morphology, functional and elemental analysis.
ii. To investigate the effect of different variables such as the chemical impregnation ratio of activated carbon, contact time, initial concentration of adsorbate and the initial temperature of solution on the adsorption efficiency.
iii. To determine the adsorption isotherm and kinetics of zinc (II) ions adsorption using mangrove-based activated carbon.
iv. To analyze the nature of adsorption process by conducting thermodynamic studies.

## 1.4 Sustainability

Sustainability is all about accomplishing our own goals without compromising the potential of future generations to fulfill their own goals. Therefore, sustainability helps in preventing the depletion of natural resources in order to make it available for a long term. Sustainability is an important element to be considered in any project. There are a total of 17 sustainability development goals (SDGs). In this research, 4 of the SDGs were achieved. Firstly, SDG no.6 which is clean water and sanitation. Undoubtedly, this research focuses mainly on industrial wastewater treatment where activated carbon is used for the removal of heavy metals present in the wastewater. This technique is carried out to improve the water quality where it is safe for consumption, reuse and ensure freshwater supplies. Apart from that, SDGs no. 7, affordable and clean energy and 12, responsible consumption and production were achieved respectively when activated carbon was prepared from renewable resource such as mangrove wood. Mangrove is abundant natural resource and is very potent to be used for synthesizing activated carbon. Besides, the application of agricultural waste to produce the precursors are generally inexpensive and environmentally friendly. As we know, the CAC is made up of non-renewable resources and require very complex and expensive processes to be synthesized. Therefore, agricultural waste must be a suitable alternative which is able to produce higher activated carbon yield. Not only that, but the degradation rate of agricultural waste is lower even during long term storage. Furthermore, SDG no.9 can be achieved because applying this method contributes to sustainable industrialization. This treatment method produces less waste and contributes to environmental waste management and sustainable long-term usage. This is because mangrove barks are produced in enormous amount which are left unused. Thus, these mangrove barks can be used for treatment purposes. Moreover, by using natural resources, the depletion of non-renewable resources like coal, lignite and fossil fuel can be minimized. Lastly, SDG no.14 which is  about conserving marine biodiversity is also achieved since the main purpose of synthesizing activated carbon for wastewater treatment is to protect the aquatic life. This is because presence of heavy metals in freshwater bodies can cause acute and chronic poisoning in the aquatic organisms.

# CHAPTER 2: LITERATURE REVIEW

## 2.1 Heavy metals in industrial wastewater

The term “heavy metals” is defined as metallic elements that are denser than water. Living organisms require heavy metals in trace amounts such as copper, cobalt, iron, manganese, zinc and molybdenum. These heavy metals are essential for human body to maintain the metabolism. For instance, manganese (Mn) is necessary for the in-vitro activation of several enzymes and is also involved in the use of glucose. Cobalt (Co) is needed as an enzyme activator, but iron (Fe) is necessary in the oxygen-carrying protein molecules in the blood. However, when the levels of essential metals exceed in a living organism, it can cause detrimental effects. When humans are exposed to excessive heavy metals, they tend to face serious health problems including slowed growth and development, nervous system damage, cancer, organ failure and even death. Lead and mercury are two metals that may contribute to the development of autoimmunity, a condition in which the immune system itself attacks a person's cells. This could cause diseases that is related to nervous system, kidneys, blood circulatory system, and damage to the fetal brain. Besides, greater dosages of heavy metals also can cause brain damage that cannot be treated (Barakat, 2011).

There are several factors that contribute to heavy metals contamination in wastewater. Industries are becoming the major source of pollutants contaminating the environment. This is because the industrial effluents containing toxic materials are discharged into water bodies without proper treatment. Industrial effluents from mining, metal ore and crude oil processing, galvanizing, medicines, insecticides, tanneries, rubber and plastics, and lumber and wood products are all point sources of heavy metal pollution in Malaysia. There are certain permissible limits for the level of heavy metals concentration in effluents from industries which is issued by the government. Table 2.1 shows the maximum allowable concentration of different heavy metals based on Environmental Quality Act 1974. The heavy metals finally reach the water bodies and contaminate the water while causing bad effects to the aquatic life. The environment may become contaminated with these heavy metals due to their non-biodegradability and pass-through food chain affecting animals and humans as well. To eliminate health risks to all living organisms, it is vital to eliminate these highly toxic heavy metals from wastewater before it is discarded.

## 2.2 Wastewater Treatment Techniques for the Removal of Heavy Metals

Heavy metals can be removed from wastewater using variety of techniques. This comprises chemical precipitation, ion-exchange, membrane filtration, adsorption, electrochemical treatment technologies and many. The advantages and limitations are evaluated to choose the best technique. Table 2.2 depicts various types of techniques used in wastewater treatment. Although all the treatments mentioned in Table 2.2 have their benefits and drawbacks in application, adsorption has emerged as a top alternative treatment technique compared to other techniques. This is because adsorption can be performed using various kinds of adsorbents. This process is more economical and feasible since the materials that are used to produce adsorbents are abundantly available. Not only that, but it is also a simple and effective process for the elimination of heavy metals from wastewater.

Table 2.1: Maximum allowable concentration of different metals in industrial effluents (Environmental Quality Act 1974).

| **Metals** | **Maximum allowable concentration in industrial effluents (mg/L)** | |
|---|---|---|
| | **Standard A** | **Standard B** |
| Mercury | 0.005 | 0.05 |
| Cadmium | 0.01 | 0.02 |
| Chromium, Hexavalent | 0.05 | 0.05 |
| Chromium, Trivalent | 0.20 | 1.0 |
| Arsenic | 0.05 | 0.10 |
| Cyanide | 0.05 | 0.10 |
| Lead | 0.10 | 0.5 |
| Copper | 0.20 | 1.0 |
| Manganese | 0.20 | 1.0 |
| Nickel | 0.20 | 1.0 |
| Tin | 0.20 | 1.0 |
| Zinc | 2.0 | 2.0 |
| Boron | 1.0 | 4.0 |
| Iron (Fe) | 1.0 | 5.0 |
| Silver | 0.1 | 1.0 |
| Aluminium | 10 | 15 |
| Selenium | 0.02 | 0.5 |
| Barium | 1.0 | 2.0 |
| Fluoride | 2.0 | 5.0 |

Table 2.2: Techniques for the removal of heavy metals from wastewater (Fu & Wang, 2011).

| TREATMENT TECHNIQUES | DESCRIPTION | ADVANTAGES | LIMITATIONS |
|---|---|---|---|
| **Chemical Precipitation** | Heavy metal ions are reacted with chemicals to generate insoluble solids during the precipitation process. Sedimentation or filtering can easily remove the precipitates from the water. The cleaned water is properly released or reused after being decanted. Traditional chemical precipitation methods for treating wastewater include hydroxide and sulfide precipitation. | 1. Relatively simple process.<br>2. Inexpensive. | 1. Produces vast amounts of low-density sludges, which is difficult to dispose of. |
| | *Hydroxide precipitation* | 1. Easy control of pH. | 1. Some metal hydroxides are amphoteric, and the ideal pH causes one metal to release the other |

| | | | |
|---|---|---|---|
| | | | metal back into the solution. |
| | *Sulfide precipitation* | 1. Precipitants do not have amphoteric properties.<br>2. Achieve a high level of metal removal across a wide pH range. | 1. Toxic hydrogen sulphide emissions are produced by heavy metal ions in acidic environments and sulphide precipitants. |
| **Ion Exchange** | Prior to exchanging the cations with the heavy metal ions present in the wastewater, ion exchange resins are utilized. Strongly acidic resins with sulfonic acid groups and weak acid resins consists of carboxylic acid groups are the most commonly utilized resins. | 1. High treatment capacity.<br>2. High removal efficiency.<br>3. Faster kinetics. | 1. Resin fouling.<br>2. Loss in ion exchange capacity over time.<br>3. Requirement of regeneration for every exchange cycle. |
| **Adsorption** | When atoms, ions, or molecules from a gas or | 1. Flexible design and | 1. Wastes formed from spent |

| | | |
|---|---|---|
| liquid attach to a solid surface, this is called adsorption. The adsorbates adhere to the adsorbent's surface by physisorption or chemisorption. They are loosely retained on the surface so that they can be easily desorbed. | operation.<br>2. High-quality treated effluent.<br>3. Low cost.<br>4. Reversible process where adsorbents can be regenerated and reused multiple times.<br>5. Diverse types of adsorbents can be utilized (low-cost adsorbents, activated carbon, bio- adsorbents, and carbon | adsorbents.<br>2. Lower selectivity. |

| | | | |
|---|---|---|---|
| | | nanotubes. | |
| **Membrane Filtration** | A process where a single feed stream passes through a semi-permeable membrane which acts as barrier and only allows certain particles to pass through. The stream separates into permeate and retentate streams after passing through the membrane. From a high-concentration area to a low-concentration area, molecules move. However, when external pressure is applied, molecules can flow from low concentration areas to high concentration areas as in reverse osmosis. | 1. High efficiency.<br>2. Can be operated easily.<br>3. Space saving. | 1. Complex process.<br>2. High cost.<br>3. Low permeate flux causes limitation in the removal of heavy metals. |
| | *Ultrafiltration (UF)*<br>Removal of dissolved and colloidal material occurs under transmembrane pressures. | 1. High metals removal efficiency through enhanced | 1. Unable to separate dissolved species and low molecular weight species. |

| | | |
|---|---|---|
| | UF membrane.<br>2. High binding selectivity. | |
| *Reverse osmosis (RO)*<br>RO utilizes a semi-permeable membrane that permits the cleansed fluid to flow through while rejecting the impurities. This is a method for removing a wide variety of dissolved organisms from wastewater. | 1. Higher ion rejection efficiency.<br>2. Simple maintenance. | 1. High power consumption.<br>2. High pumping pressures.<br>3. Requirement of membrane restoring procedures. |
| *Nanofiltration (NF)*<br>The rejection of heavy metal ions is aided by this intermediary phase between UF and RO. | 1. Ease of operation.<br>2. Reliable.<br>3. Low energy consumption.<br>4. High efficiency of pollutant removal. | 1. High energy consumption.<br>2. Soluble elements cannot be separated. |

| | | | |
|---|---|---|---|
| **Electrochemical treatment** | This is the process of metal ions plating out on a cathodic surface. Metals in their elemental condition can be recovered using this method. | 1. There are no lingering residues.<br>2. It is quick and well-controlled, and it uses fewer chemicals.<br>3. Reduce the amount of sludge produced. | 1. Larger capital investment.<br>2. Expensive electricity supply.<br>3. High maintenance and operation cost. |
| **Coagulation and Flocculation** | By reducing the forces holding colloids apart, the process of coagulation destabilizes the colloids. Hydrophobic colloids and suspended particles are major components that coagulate. The process where polymers create connections between flocs and bind the small particles into massive clumps is known as flocculation. Filtration or floating can be used to separate these aggregates. | 1. Good sludge settling.<br>2. Good dewatering characteristics. | 1. High chemical consumption.<br>2. Increased sludge volume generation. |

## 2.3 Adsorption Process

The term adsorption refers to a process of mass transfer in which a specific material is moved from a liquid or gaseous phase to the solid phase's surface. Chemical and physical reactions bond the materials to the surface of the solid. The solid phase is referred to as the adsorbent, while the material connected to it is referred to as the adsorbate. In this research, the pollutants such as heavy metals in wastewater that adhere to the solid surface are the adsorbates. Porous solid particles with tiny diameters or linked pores are utilized to increase the surface area for adsorption per unit volume (Seader et al., 2011). The mechanism of adsorption process is shown in Figure 2.1. The solute diffuses from bulk fluid to the adsorbent's exterior surface in this process. The solute travels through the liquid film that is bonded to the surface of the solid and is adsorbed onto the surface, where it undergoes surface reaction. Once the adsorbent is saturated with adsorbates, regeneration of adsorbent is done through desorption of sorbed substances from the surface (Seader et al., 2011).

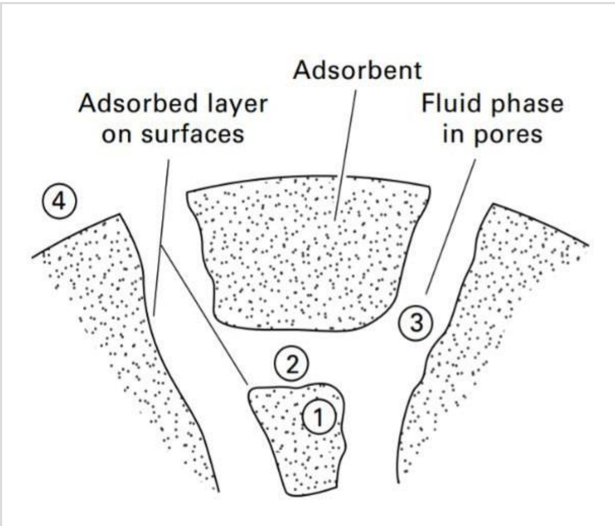


Figure 2.1: Mechanism of adsorption (Seader et al., 2011).

Generally, adsorption can be classed as either physical (physisorption) or chemical (chemisorption) depending on the forces that present between the fluid molecules and the solid surface. Physisorption occurs when the solutes are retained onto the adsorbent by van der Waals forces. Physisorption occurs rapidly and may consists of mono-molecular (unimolecular) layer, or two or more layers thick (multimolecular). The unimolecular layer formation contributes to reversible process. When multimolecular layer is formed, it may result in hysteresis where the capillary pores are filled. Firstly, adsorption begins with monolayer, and becomes multilayered. Capillary condensation begins when the pores formed on the adsorbent approach the size of molecules, and the pores are eventually filled with adsorbates. As a result, a porous adsorbent's maximum capacity is proportional to pore volume rather than surface area (Seader et al., 2011). However, these binds can be freed easily by applying external energy such as heat.

Meanwhile, when the forces of attraction present between solutes and adsorbent in a monolayer involves chemical bond, it is known as chemisorption. This process often involves a release of heat larger than the heat of vaporization (Seader et al., 2011). In addition, the bond formed is irreversible due to its stronger strength and it is highly specific with requirement of activation energy. Chemisorption takes place predominantly at higher temperatures compared to physisorption.

## 2.4 Activated Carbon as Low-cost Adsorbent

Recently, several low-cost adsorbents have been introduced and used for removing heavy metals from industrial effluent. These materials were generated from natural materials, industrial by-products, agricultural waste, or modified biopolymers (Barakat, 2011). The most widely used adsorbent is activated carbon (AC)

(Bhatnagar et al., 2013). The phrase "activated carbon" is frequently used to refer to carbon-based materials that also contain a well-developed interior pore structure. Their application in the elimination of heavy metals from wastewater is because of having large mesopore and micropore volumes which contributes to higher surface area for adsorption (Fu & Wang, 2011). However, the conventional AC which is coal-based is very expensive. Therefore, much research has been conducted to synthesize AC from agricultural wastes which makes it a suitable adsorbent that is inexpensive.

Typically, agricultural waste such as rice husk, sawdust, palm shell, coconut shell, urban organic waste, fruit peels and tree barks are used as feedstocks to synthesize AC because they are present generously in nature, lower in cost and only need simple processing. Other than that, according to many studies throughout the years, utilizing biological waste as a feedstock for synthesizing AC also contributes to environmental waste management. A study was conducted for the synthesis and characterization of mangrove-based AC (Saha, 2016). In this research, highly porous AC was synthesized through potassium hydroxide (KOH) activation. The mangrove-based AC possessed higher surface area (2830 $m^2$ $g^{-1}$ ) and pore volume (1.90 $cm^3$ $g^{-1}$). In 2018, Caroline and Kusuma, performed water treatment using AC derived from mangrove roots. AC is also derived from many parts of mangrove such as mangrove propagule, mangrove wood, mangrove fruit and mangrove roots (Caroline & Kusuma, 2018). Furthermore, *Mucuna pruriens* seed shells were also used to produce AC to treat textile wastewater (Igwegbe et al., 2016). The activated Mucuna pruriens seed shells were discovered to be a powerful adsorbent to treat wastewater which contains congo red and malachite green, according to the research. The AC derived from rice husk showed high adsorption capacity of 58.08% and highest carbon yield of 47.75% (Hanum et al., 2017). Not only that, a study with banana peel derived

AC also showed good efficiency for adsorption heavy metals at higher concentrations (van Thuan et al., 2017).

From all the studies that have been conducted, it can be observed that agricultural wastes such as mangrove barks make an ideal feedstock for the synthesis of AC. This is because mangroves are a dominant ecosystem in Malaysia. In the tropics and subtropics, mangroves thrive in brackish water and saline soil that is subject to fresh and saltwater inundation on a regular basis. Mangroves have specific adaptations that allow them to live in their natural habitat, such as robust root systems, unusual structures of bark and leaves, and other unique characteristics. The most well-known mangrove trees are those of the genus *Rhizophora*, which belongs to the family *Rhizophoraceae* and is a genus of tropical mangrove trees. Not only that, but mangrove forest is a highly productive ecosystem that provides resources to coastal people and serves as a breeding ground for diverse types of marine creatures such as fish, prawns, and crabs. Besides, mangroves serve as a natural filter, retaining, concentrating, and recycling nutrients as well as removing toxicants. Mangroves are harvested mainly for piling purposes while their timbers are utilized for the production of charcoal, firewood and woodchips. As a waste, mangrove barks are generated in a large amount which are left unused. The barks contain highest phenolic content and are able to retain high amounts of char (de Ramos et al., 2019). Accordingly, the phenol groups act as an active species in the adsorption process.

## 2.5 Preparation of Activated Carbon

Carbonization and activation are the two processes in the preparation of AC. To make char, carbonization is accomplished via pyrolysis or gasification at higher temperatures with an inert atmosphere. The carbon content of the char is created by thermal decomposition of volatile matter, non-carbon species such as nitrogen, hydrogen and oxygen. Furthermore, the devolatilization process results in development of pore structures of precursors (Heidarinejad et al., 2020). During the carbonization process, the heating rate, the carbonizing temperature, flow rate of gas supply and the residence time are important parameters to be considered. For instance, when the temperature of carbonization rises, it releases more volatile species, raising the content of ash and fixed carbon.

The activation step on the other hand is a crucial process. This is because it influences the characterization of the AC which affects the adsorption performance as well. There are two types of activation process which are physical and chemical activation. Generally, physical activation comprises two steps, firstly, carbonization of dried precursors occurs at 400-700°C to produce char. The process continuous with the activation in oxidizing environment containing steam, air, $CO_2$ or mixtures of air with increasing temperatures about 800-1100°C (Reza et al., 2020). The synthesize of char through carbonization produces tarry substances which get filled in the pores of the char lowering its surface area and adsorption capacity. Consequently, physical activation is encouraged to remove the tarry substances, widen the pores and develop new pores as well. This enhances the surface area and porosity of the carbonaceous porous structure.

Next, chemical activation might be single-staged or two-staged. In a single-stage chemical activation process, carbonization is not carried out, meanwhile the dried precursor is activated by several chemical reagents such as NaOH, KOH, $ZnCl_2$, or $H_3PO_4$. During the two-stage process, the dried precursor is first carbonized to produce biochar at a temperature of 400- 600°C, before undergoing chemical activation. The different types of chemical activation involve basic, acidic and neutral activation (Reza et al., 2020). The surface properties and quality of AC are highly influenced by activation conditions, type of activating agents and impregnation ratio. Table 2.3 shows various activation techniques to synthesize activated carbon by several research.

Generally, activation is carried out via conventional heating. However, due to its selective, rapid, even, and volumetric heating, as well as its indirect connection between the heating foundation and heated resources, microwave activation has gained a lot of interest as a substitute approach for activation (Reza et al., 2020). Not only that, but the activation time is also reduced through microwave activation. In microwaves, heat is generated from the reorientation of molecules. Microwave irradiation associates directly with the particles contained in the material, converting electromagnetic energy to heat transfer within dielectric materials (Hesas et al., 2013). Meanwhile, in a conventional furnace, the heat is transferred through furnace walls which creates a temperature gradient through the samples having different shapes and sizes (Namazi et al., 2016). This is because the energy from heating is transferred to the sample which is being activated from the inward surface to its interior by conduction, convection and radiation. A longer heating duration is required to eliminate the temperature gradient and reach desired temperature of activated material, which also increase the cost and energy consumption. Figure 2.2 represents the schematic diagram that shows the principle of conventional and microwave heating.

Besides, the advantage of microwave heating is that the temperature gradient is not present. This is due to the fact that microwaves transmit heat as electromagnetic waves, which can transfer a significant quantity of heat to the inside of the substance being activated. Not only that, dipole rotation and ionic reduction convert the microwave energy received into heat within the particles (Alslaibi et al., 2013). Next, microwave furnaces are smaller in size compared to conventional furnaces. Microwave heating also enables immediate startup and shutdown and improved safety as well. The consumption of gases for the activation of carbon sources can be reduced by using microwave heating due to shorter treatment time is required. However, microwave radiation can cause hot spots inside the carbon particles due to the presence of mineral impurities. Therefore, the temperature is substantially greater than the average temperature. Due to the temperature difference, heterogeneous interactions between the inert gases used in the process and the precursor are frequent. The sample's inner temperature could be tens or hundreds of degrees larger than its exterior because of the interior and volumetric nature of microwave heating (Hesas et al., 2013).

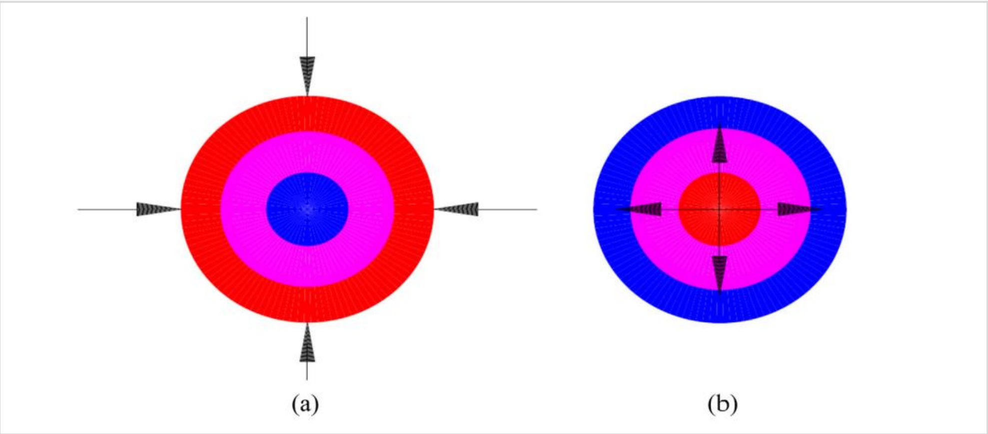


Figure 2.2: Schematic diagram of temperature profile and direction of heat transfer (a) Conventional heating (b) Microwave heating (Red-high temperature, blue-low temperature) (Ao et al., 2018)

Table 2.3: Summary of activation techniques and different activating agent used for activated carbon derived from various carbon sources from different literatures.

| **Activation Technique** | **Raw Materials** | **Activating agent** | **Max Adsorption Capacity ($Q_{max}$) (mg/g)** | **References** |
|---|---|---|---|---|
| Conventional | Jatropha hull | Steam | 950 | (Xin-hui et al., 2011) |
| | | $CO_2$ | 1008 | |
| | Mangrove fruit waste | KOH | 1540.13 | (Paryanto et al., 2019) |
| | Durian peel | $CO_2$ | 284.00 | (Nuithitikul et al., 2010) |
| | Piassava fibers | $ZnCl_2$ | 276.40 | (Avelar et al., 2010) |
| | Rice straw (*Oryza sativa L.)* | Citric acid | 68.7 | (Wang et al., 2019) |
| Microwave | Jatropha hull | Steam | 988 | (Xin-hui et al., 2011) |
| | | $CO_2$ | 998 | |
| | Orange peels | $K_2CO_3$ | 379.63 | (Foo & Hameed, 2012) |
| | Cotton stalk | $ZnCl_2$ | 193.50 | (Alslaibi et al., 2013) |
| | Apple pulp | $H_3PO_4$ | 283.8 | (Hesas et al., 2013) |
| | Apple peel | $H_3PO_4$ | 277.8 | |
| | Bamboo | $H_3PO_4$ | 286.10 | (Liu et al., 2010) |
| | Pine wood powder | $ZnCl_2$ | 200.00 | (Wang et al., 2019) |