STUDY OF LOW COST BIOSORBENT COCOS. NUCIFERA L. (COCONUT) SHOOT FOR BIOSORPTION OF NICKEL

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering

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April 2020

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"STUDY OF LOW COST BIOSORBENT COCOS. NUCIFERA L. (COCONUT) SHOOT FOR BIOSORPTION OF NICKEL"** was prepared by **BRENDA LIM AI-LIAN** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering at Universiti Tunku Abdul Rahman.

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ACKNOWLEDGEMENTS

I would like to thank everyone who had contributed big or small to the successful completion of this final year project. I would like to express my deepest gratitude to my research supervisor, ChM. Ts. Dr. Tee Shiau Foon and Ts. Dr Shuit Siew Hoong for their invaluable advice, guidance and enormous patience that had led me to successfully complete this project.

In addition, I would also like to express my gratitude to my loving parents and siblings who had been giving me continuous emotional support and insights during times when I felt unmotivated or down. Besides, I would like to thank my friends who had given me a helping hand and advices when needed during laboratory sessions.

On the other hand, I would like to thank the lab officers who had been patiently and willingly tending to all my lab related needs and requirements. Lastly, I would like to offer my sincere regards to those who had supported me throughout this journey to the completion of this project.

ABSTRACT

Nickel is a toxic heavy metal whereby its presence in high concentration than allowed in water or wastewater are of great concern. Many conventional removal methods of nickel were either costly or less efficient. Biosorption was currently a favourable alternative in the removal of heavy metal or organic pollutants while *Cocos Nucifera L.* shoot was a biowaste often disposed of. This study was executed to examine the efficiency of the *Cocos Nucifera L.* (Coconut) shoot as a low cost biosorbent on the biosorption of nickel from water. The optimum conditions for the biosorption of nickel using *Cocos Nucifera L.* shoot were determined through experiment. The influence of few parameters on the biosorption of nickel were analysed individually such as pH, biosorbent (*Cocos Nucifera L.* shoot) dosage, biosorbate(nickel) concentration, contact or agitation time as well as size of biosorbent. The highest percentage of nickel removal were obtained at pH 9 (82.55%), 30 minutes contact time (87.91%), 25 g of biosorbent dosage (89.56%), and biosorbent size of 300 to 850 µm (90.872%). In accordance to the experimental outcome, Langmuir isotherm along with the Pseudo-Second Order Kinetics were found to best describe the biosorption of nickel by *Cocos Nucifera L.* shoot with their correlation coefficient (R^2) values of 0.995 and 0.9906, respectively, indicating that monolayer biosorption with second order mechanism takes place on the *Cocos Nucifera L.* shoot. Characterisation of *Cocos Nucifera L.* shoot before and after biosorption using SEM-EDX and XRD showed that nickel was absorbed after biosorption. In conclusion, *Coco Nucifera L.* shoot was suitable to be utilised as an affordable biosorbent to withdraw nickel from water or wastewater.

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C_e	equilibrium concentration of metal ions (mg/L)
$C_{m/}C_0$	initial concentration of metal ions (mg/L)
HY	number of acid sites on surface of solid
k_1	rate constant of pseudo first order mechanism
k_2	rate constant pseudo second order mechanism
K_L	Langmuir equilibrium constant
K_f	adsorption capacity (Freundlich constant)
K_{IE}^H	equilibrium constant of the ion exchange mechanism
M	dry mass of biosorbate added (g)
M^{X+}	metal ion
MY_X	sorbed metal ion
n	Freundlich constant
q_e	amount of metal ions biosorbed at equilibrium (mg/g)
q_m	maximum biosorption capacity (mg/g)
q_t	amount biosorbent adsorbed at time t (mg/g)
R_L	favourability of the isotherm
R^2	linear correlation coefficient of isotherm
V_0	initial volume of stock solution (L)
V_e	equilibrium volume of stock solution (L)

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

The condition of the environment worldwide has been continuously changing for the worst. Decades ago, the air was fresher and the river as well as ocean water were cleaner. Currently, there are traces of pollutions that can and cannot be seen with naked eyes. Pollutions that can be spotted with naked eyes are such as plastic wastes, and oil spill found in the seas, rivers, ocean, and even by the roadside. On the other hand, pollutions that are failed to be noticed with naked eyes are those that are so small in size that one is unable to sense its presence in the environment. These kinds of pollution were only able to be detected by using special equipment or only when unpleasant effects of the pollution on human health and the environment had occurred. It changed the conditions of the environment for the worst (UN Environment, 2018). Such pollution includes acid, heavy metals, and other elements that are in excess concentration than allowed. As time goes by, the industry continues to revolve while the environment quality degrades.

Heavy metals familiarly known as crucial trace elements have been extensively scattered in the environment. Heavy metal are metals from the periodic table with density and atomic mass higher than other types of metal (Koller and Saleh, 2018). At present time, it can be observed that there is a rise in the worldwide concern on the possible detrimental impact that heavy metal may have on the wellbeing of human beings and animals as well as its adverse impacts on the ecosystem. Although natural phenomena have a fair share of contribution to the pollution of heavy metal, anthropogenic activities had greatly surged the richness of heavy metals discovered in Mother Nature (RoyChowdhury, Datta and Sarkar, 2017).

Nickel is within the class of heavy metals mentioned above. It can be detected in different forms in the air, soil and water (Rathor, Chopra and Adhikari, 2014). All human beings may be exposed to nickel as it can be found in the waters, soil, drinking water, in jewelleries we wear daily, and even in the food (Das et al., 2019).

Among the major heavy metal pollution cases that happened recently in Malaysia, reportedly in May 2019, was the contamination of the waters with heavy metal such as lead, cadmium as well as nickel in the coastal area Teluk Bahang, Penang. Studies carried out by *Universiti Sains Malaysia (USM)'s Centre for Marine and Coastal Studies (*CEMACS*)* had shown that the nickel concentration found in the waters near the Penang National Park and fish farms allocated in Teluk Bahang were 1038 % and 982 % higher than natural in seas (Sekaran, 2019). The contamination of the heavy metals in the sea waters had affected the quality of the water whereby the dissolved oxygen (DO) was as low as 0.08 mg/l, jeopardizing the marine life and business of fisheries, whereby tonnes of fishes were found dead.

Currently, there are many techniques and technologies applicable for nickel pollution management (Joshi, 2017). However, these methods may be costly when carried out at a large scale. Hence, researchers were slowly shifting their studies into looking for environmentally friendly, efficient yet low cost absorption substitutes to replace conventional materials and techniques.

1.2 Importance of the Study

It is a necessity to implement improving detection standards and treatments of heavy metal pollution. The never-ending increase in heavy metals concentrations in the environment continues to cause adverse effects on the ecosystem. As most industrial treatment desire to inhibit as well as to curb the discharge of toxic, this would require additional expenditure. Hence, it is important to study possible low cost and yet environmentally friendly methods in reducing the heavy metal pollution.

Nickel was chosen as the targeted biosorbate for this study due to the fact that there is an alarming increase in nickel pollution around the world, including Malaysia. Even at a low concentration, the presence of nickel is still considered as unsafe due to its carcinogenic characteristic. Hence, it is essential to put in all effort in the removal of nickel from the atmosphere as well as to prevent further increase in its concentration in the atmosphere, in order to protect the health of the human beings, flora as well as fauna.

This study held great importance to investigate on the biosorption efficiency of the *Cocos. Nucifera L.* (coconut) shoot as a biosorbent. The *Cocos.*

Nucifera L. shoot was used to remove nickel ions that are known to be a pollutant when found excessive. As researchers were keen to discover new possible biosorbents that were known to be easily available and low cost yet efficient, this study serves to analyse *Cocos. Nucifera L.* shoot 's efficiency in the removal of nickel, for it to be classified as a good biosorbent for nickel.

In the future, this study may perhaps be useful for further researches on the removal of nickel through biosorption at an industrial scale. Besides, this method of heavy metal can be implemented as a substitute to conventional techniques and technologies especially in developing countries with lack of funding or resources. Not only does it helped to save cost while reducing nickel pollution, it also helped to reduce agricultural waste.

1.3 Problem Statement

Nickel in excess is harmful towards human and animals as well as plants (Shuhaimi-Othman et al., 2012). Thus, it is a necessity to minimize the concentration of nickel to the limit that is implemented by the authorities. There were many conventional technologies that were commercially implemented to remove nickel from aqueous solutions. Nevertheless, these methods were not economical and may be very costly to implement in the industry and may not fit into the budget of all the industrial companies (Joshi, 2017). There were a lot of studies on the biosorption method with a large variety of biomass as biosorbents. However, the biosorption methods that were studies were not implemented in the industry as they were not as commercialised as the conventional technologies (Shamim, 2018).

In order to study the performance as well as the mechanism of the biosorption process of the *Cocos Nucifera L.* shoot, its surface morphology and its elemental information must be known. As there was no research done on the *Cocos Nucifera L.* shoot before, such information were hard to come by. Besides that, there was no standardized operating condition for biosorption process to take place. Each biosorbent had its own efficiency of biosorption and its efficiency was also affected by the operating conditions. The biosorption mechanism and efficiency of each biosorbent may differ from one another. Thus, the biosorption efficiency of the *Cocos Nucifera L.* shoot cannot be determined from the work of other researchers on other types of biosorbents. As different biosorbents possessed different surface morphology, functional group, and element, each biosorbent may have its own mechanism or combination of mechanisms of the biosorption process. Hence, the kinetic and isotherm model to illustrate the biosorption mechanism was unknown.

1.4 Aim and Objectives

The leading aim of the study is to investigate the efficiency of *Cocos Nucifera L.* shoot as a biosorbent in the biosorption of nickel from aqueous solution. To accomplish the aim of the study, there are several objectives to achieve such as:

I. To characterize *Cocos Nucifera L.* shoot before the adsorption of nickel from aqueous solution.
II. To determine the effect of pH of solution, biosorbent dosage, contact time, initial metal concentration, and biosorbent size as well as to find the optimum condition for the biosorption of nickel from aqueous solution.
III. To evaluate on the efficiency of *Cocos Nucifera L.* shoot on the removal of nickel from aqueous solution.
IV. To identify the kinetic and isotherm model to illustrate the biosorption mechanism of nickel.

1.5 Scope and Limitation of the Study

In this study, the shoot of the *Cocos Nucifera L.* is used as a low cost biosorbent in the biosorption of nickel from aqueous solution. Several scopes of study that were proposed in the direction towards achieving the objectives of this study are:

I. Characterize and understand the biosorbent in terms of surface morphology, functional group, and elemental information.
II. Analyse the effect of pH of solution, biosorbent dosage, contact time, initial metal concentration in solution and biosorbent size in the experiment.
III. Analyse the efficiency of removal of biosorbate by biosorbent.
IV. Analyse the result of the experiment by applying kinetic study and models that illustrates the biosorption mechanism of nickel.

The main limitation of this study is that there is no research done on *Cocos Nucifera L.* shoot itself and as a biosorbent. This study has to be done by reviewing researches done on other material as biosorbent for the removal of nickel. Due to limited time and equipment, only several parameters such as pH of solution, biosorbent dosage, biosorbent size, contact time and initial metal concentration, as well as characteristics had been studied on *Cocos. Nucifera L.* shoot as a biosorption material.

1.6 Contribution of the Study

The optimum parameters of the biosorption of nickel by using *Cocos Nucifera L.* shoot as biosorbent obtained can be used as reference for future researches. The characterisation carried out in this study can also be used as primary reference as there are currently no other researches done on *Cocos Nucifera L.* shoot that can be found. Besides, it can also be a reference for researches for the study of other type of biosorbent. The findings of this study can be a starting point for further research for further improvement on *Cocos Nucifera L.* as a low cost biosorbent to be used in the industry in the near future.

1.7 Outline of the Report

This report comprises of five major chapters which includes the introduction, literature review, methodology, result and discussion, as well as the conclusion along with the recommendations for this study. The introduction chapter briefly describes the reason and aim of carrying out this study. The literature review chapter are collected principles, knowledge and findings of the research carried out for this study. With the knowledge and findings collected from various studies by different researches, a suitable work plan and methodology to carry out the preparation of materials and experimental setup as well as characterisation were fabricated to suit the purpose of this study. After carrying out the experiment and characterisation, the results were analysed and discussed in the results and discussion chapter. A conclusion was made with several recommendation for improvement of this study were deduced in the last chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metal

Heavy metals are natural elements that can found naturally in rocks as well as the earth crust. These elements are called heavy metals due to their atomic mass and density which are higher in comparison to water (Tchounwou, et al., 2012). An element with density higher than 5g/cm^3 would have been characterized as heavy metals and hence, separating them from other 'light' metals (Koller and Saleh, 2018).

2.1.1 Sources of Heavy Metal

The root cause of heavy metals found in the environment are classified into natural phenomenon as well as anthropogenic activities. Natural cause of heavy metal pollution involves corrosion of metal, eruption of volcano, leaching as well as erosion of soil (Joshi, 2017). On the other hand, anthropogenic activities contribute significantly to the rise in heavy metal accumulated in the ecosystem. Examples of anthropogenic activities which resulted in an increase of heavy metal within the environments are such as combustion of fossil fuels, combustion of coals, heavy metal mining, emission from nuclear power plants, agricultural activities and industrial effluent disposal (Ilyin, et al., 2018).

2.1.2 Heavy Metal Pollutions and its Effect

Heavy metal water contamination is a global leading concern and challenge. These contaminants in water bodies had become the leading source of pollution. The most common contaminants are such as copper, zinc, iron, lead, nickel cobalt, mercury, cadmium, arsenic, and manganese (Joshi, 2017).

In recent decades, there were several journals in which its studies were executed on the heavy metal contamination in Malaysia. Shazili, et al. (2006) had performed a study on the severity of heavy metal pollution of the marine ecosystem in Malaysia. It was found that the main contributors of heavy metal in the waters of Malaysia are the manufacturing industry, agricultural industry, sewage as well as emission from motor vehicles. According to Shazili *et al.*,

(2006) in the Straits of Malacca, shipping and port activities are the primary cause of lead, copper, and arsenic pollution. In addition to that, he had also mentioned that there were traces of lead, copper and zinc in the river sediments that receives considerable amount of pollution from industries, sewages and runoffs (Shazili, et al., 2006).

Ripin, et al. (2014) had analysed and assessed the heavy metal pollution in soil in the state of Perlis. The concentration of several heavy metals was analysed by using the Pollution Index (PI). It was analysed that the concentration of chromium, nickel and lead was lower than the allowable limit whereas the concentrations of copper and cadmium had exceeded the allowable concentration limit in soil (Ripin, et al., 2014). It was deduced that the primary source of copper, cadmium and lead in the soil of Perlis were vehicle emission as well as industrial activities. To contradict that, Ripin, et al. (2014) had disclosed that nickel and chromium come from natural sources.

Another study in which the build-up of heavy metal in fishes in the Terengganu Coastal Area was analysed, was conducted by Rosli, Samat, Yasir and Yusof , (2018). It was found that the average concentration of iron found in the fishes had exceeded the limit of the recommended dietary allowance (RDA) while other metals including zinc, copper, manganese, cadmium and lead were below limit. However, Rosli, Samat, Yasir and Yusof concluded that consumption of the fishes would not cause any acute toxicity to human.

Heavy metals dissolved in aqueous solutions causes a major environmental issue due to its toxicity which human and animals and plants can be exposed in many forms including the intake of food with heavy metal deposition (Joshi, 2017). Although at low concentration, most heavy metals that are released through wastewater are found to be toxic and carcinogenic which causes great damage the to human health (Duda-Chodak and Błaszczyk, 2008). The toxicity of heavy metals is so dangerous such that it could inflict harm to the central nervous system, gastrointestinal system, cardiovascular system, bones, endocrine gland, lungs, liver as well as the kidneys (Joshi, 2017). High exposure to heavy metals had been said to be the cause of some physiological degeneration diseases as well as the heighten risk of cancer (Hima, et al., 2007).

These contaminants can be characterised into two types, namely the essential or non-essential trace metals. Essential heavy metals, such as copper, manganese, selenium, chromium, cobalt, and many others, are those that possess of functions that are very important biologically in living things (Tchounwou, et al., 2012; Sathawara, Parikh and Agarwal, 2004). These elements are vital in many biological systems as well as to herds the whole metabolism of living things (Mertz, 1981).

Cobalt plays a role as a central atom in vitamin B12 complexes (Koller and Saleh, 2018). It is an important part of the reductive branch of propionic acid in the fermentation process. Zinc is important for many types of enzymatic activities (Rengel, 2004). These enzymes include isomerase, polymerases of DNA and RNA, dehydrogenases etcetera. The activity of these enzymes stops when zinc is removed which are found in the functional group of the molecule. According to Rengel (2004), the amount of enzymes in a plant drops drastically if there is a deficiency in zinc. However, excessive intake of zinc would result in acute adverse effects. Magnesium is also an essential element for the flora and fauna such that lack of this element would cause abnormalities in the mammal reproductive and skeletal system (Wilkinson, et al., 1987). Koller and Saleh, (2018) stated that copper portrays a big part on the growth and metabolism of living things.

On the other hand, non-essential trace metals are those that are toxic even in a small amount(Koller and Saleh, 2018). These non-essential trace metals include chromium, nickel, lead, cadmium, mercury and etcetera (Koller and Saleh, 2018; Arief, et al., 2008). As an example, high concentration of cadmium would affect the pulmonary function while that of lead would cause serious harm to the central nervous system, liver and kidney. Table 2.1 shows several health effect of non-essential element heavy metal.

Table 2.1 Health Effect of Heavy Metal

Heavy Metal	Health Effect	Reference
Chromium	Headache, vomiting, diarrhea, haemorrhage, possible modification in DNA transcription, skin allergy and cancer, ulcer in nasal septum	Jaishankar, *et al.*, 2014
Zinc	Depression, seizure, anaemia, skin irritation, lethargic, dehydration	Arief, *et al.*, 2008, Kumari and Sharma, 2017
Lead	Mental retardation, low haemoglobin production, seizure, kidney problem, miscarriage, infertility, Lead poisoning	Jaishankar, *et al.*, 2014, Kumari and Sharma, 2017
Copper	Wilson's disease, insomnia. Damage of liver	Arief, *et al.*, 2008
Nickel	Nausea, asthma, allergy, dermatitis, gastric, cancer	Arief, *et al.*, 2008

2.2 Nickel

2.2.1 Nickel Properties and Its Application

Nickel which is a hard and ferromagnetic metal is one of the many trace heavy metals that are extensively spread in the ecosystem (World Health Organization, 2005). It is placed at 24th as the most abundant element where by it contributes up to 6% of the earth's core content (Agency For Toxic Substances and Disease Registry, 2005). It is found naturally as a component of soil and groundwater at below 100ppm and 0.05 ppm, respectively (Rathor, Chopra, & Adhikari, 2014). In the environment, it is mostly found as sulphides or oxides as it combines with sulphur and oxides (Agency For Toxic Substances and Disease Registry, 2005). Nickel occurs primarily in natural waters in the form of $Ni(H_2O)_6^{2+}$ ion when the water is conditioned at 5 to 9 pH (Rathor, Chopra and Adhikari, 2014). Nickel and nickel compounds are colourless and tasteless. Nickel compounds such as are rather soluble in water, and possesses a distinctive green colour

(Agency For Toxic Substances and Disease Registry, 2005). It is also discovered as sea floor nodules on the ocean floor in the form of mineral lumps as well as in meteorites.

Nickel possesses properties which advantageous to form mixtures with other types of metals, such as chromium, iron, zinc and copper (Agency For Toxic Substances and Disease Registry, 2005). It is widely used in the production of super alloys, Ni-Fe alloys, stainless steels, catalysts, electroplating materials, batteries, coins, jewellery and many more metallic object or materials used in the industries and our daily life (Rathor, Chopra and Adhikari, 2014). There are also nickel compounds found in which nickel combines with other elements such as chlorine, oxygen as well as sulphur. Nickel compounds are utilized in the production of nickel plating, batteries, catalyst as well as to colour ceramics (Agency For Toxic Substances and Disease Registry, 2005). Not only that, nickel is also utilized as a raw material in food industries, as well as metallurgical. Nickel is also added in some food supplements whereby its content can be as much as several milligrams in each tablet (Agency For Toxic Substances and Disease Registry, 2005). Although it is a fundamental element for plant growth at a low concentration, it is toxic to be consumed by the human body.

2.2.2 Nickel Pollution and its Sources

Nickel pollution could be resulted from either natural phenomenon or anthropogenic activities. Natural phenomenon especially volcano eruption releases nickel into the environment and hence, increasing the concentration of nickel. Anthropogenic activities play a major role in the nickel pollution we face today. Examples of these activities include metal mining, vehicle emission, organic manures, fertilizers, as well as the municipal, industrial and household wastes disposals (Rathor, Chopra and Adhikari, 2014)

2.2.2.1 Air

The main sources of nickel pollution in air are activities that involve burning. Furnaces used for alloy making, coal-burning and oil-burning power plants as well as rubbish incinerators release nickel into the environment (Agency For Toxic Substances and Disease Registry, 2005). Nickel released from the stack of furnaces adheres on small dust particles in the air. These dust particles settle to the ground or are being removed from the air through rain or snow. When released into the atmosphere, nickel that sticks onto dust particles usually take several days to be taken out from the air (Agency For Toxic Substances and Disease Registry, 2005). In the case of nickel that adheres on very small particles, it is usually more difficult to remove and may take up to a month to be removed from the air. The air in industrial or waste treatment area tends to have higher content of nickel (Cempel and Nikel, 2006). Emission of vehicles also contributes a fair amount to nickel pollution in air.

2.2.2.2 Soil

The concentration of nickel in groundwater depends greatly on the type of soil, its pH as well as the depth of which the sampling was extracted (World Health Organization, 2005). On average, the concentration of nickel in soil is normally within the stretch of 4 to 80ppm (Agency For Toxic Substances and Disease Registry, 2005). The distribution of nickel in soil is frequently uniform. However, it is commonly accumulated on the soil surface as a result of the discharge from agriculture as well as industrial activities (Cempel and Nikel, 2006). It was reported that the concentration of nickel had increased in municipal tap water as well as groundwater (Rathor, Chopra and Adhikari, 2014). The increase in mobility of nickel in the soil as well as the concentration of nickel in groundwater may be resulted from acid rain(Agency For Toxic Substances and Disease Registry, 2005). In acidic condition, the mobility of nickel in soil is greater and hence, nickel tends to seep leak into groundwater. Large portions of nickel that are dispersed into the environment are found in sediment or soil whereby nickel strongly adheres to manganese- and iron-containing particles (Agency For Toxic Substances and Disease Registry, 2005).

2.2.2.3 Food

Food is a major exposure media of nickel to the human population (Agency For Toxic Substances and Disease Registry, 2005). In boiled water, the content of nickel is dependent on the material of the heating element. An extreme case of high nickel content of up to 1000mg/L in boiled water was reported (World Health Organization, 2005). In new stainless steel pipes utilized for drinking water, the nickel concentrations leached from the pipe were up to 6µg/L (Nickel Development Institute, 2004). Dissolved nickel can be found in acid beverages and soft drinks due to the leaching of nickel from containers and piping (Das, et al., 2019). In cases whereby the pipes were joined to gunmetal and tinned copper fittings, the maximum concentration of nickel would increase. The concentration of nickel in bottled mineral water relies on the source of water and the treatment used. It was recommended by the World Health Organization that the allowable maximum nickel concentration in drinking water is not more than 0.07mg/L (Guyo, et al., 2016).

Much to our dismay, the food consumed by human beings contains nickel generally within the range of 0.1 to 0.5 mg/kg (Cempel and Nikel, 2006). Cooking utensils made of stainless steel makes a remarkable contribution to the nickel found in cooked food, in which the nickel concentration found in meat exceeds 1mg/kg meat sometimes (Dobeka and Mckenzie, 1995). On contrary to that, it was found by Flint and Paikirisamy (1995) that there was only a small increase in the concentration of nickel in acidic food when stainless steel utensils were utilized. There are certain foods that naturally have high content of nickel such as oatmeal, nuts, chocolate and soybeans (Cempel and Nikel, 2006). High nickel content were detected in nuts and beans as well as seed at 1 to 6 mg/kg (World Health Organization, 2005).Vegetarians are expected to have consumed greater amount of nickel ranging from 0.06 to 0.26 mg/kg, due to their intake of nuts and beans as their main source of protein. This due to the higher content of nickel in vegetables compared to other food items (Das, et al., 2019).

2.2.2.4 Water

In accordance to the United States Environmental Protection Agency, the advised nickel content allowed in wastewater would be not more than 0.5mg/L (Guyo, et al., 2016). In water or wastewaters, nickel can be found attached on suspended materials in water, or dissolved in water as its own. Industries that produces or utilize nickel, nickel compounds or nickel alloys may also contribute to nickel pollution through discharge of nickel in wastewaters (Idriss and Ahmad, 2013). Excess nickel found in the soil or waters may be due to leaching from metals in which they are in contact with, such as pipes and fittings. Other than that, it could be due to nickel ore-bearing rocks.

The Straits of Malacca is known to be an international dominant shipping lane and its nautical activities contribute to the nickel contamination in Malaysia (Shazili, et al., 2006). The developing oil and gas industries concentrated in the east coast of Malaysia also affect the concentration of nickel in the waters. According to Shuhaimi-Othman, et al. (2012), Malaysia does not have adequate water quality criteria standards (WQCs) that are based on the biota of local aquatics. WQCs that are currently available for heavy metals in Malaysia are based on standards and criteria of other countries in which the condition of the environment differs from that of Malaysia (Shuhaimi-Othman, et al., 2012). There is a vast difference between the taxonomic composition of the waters in Malaysia and the countries in which the WCQs were developed for.

2.2.3 Effect of Nickel Toxicity

2.2.3.1 Effect on Human

A person may be exposed to nickel in many ways such as breathing air, smoking tobacco that contains nickel, or drinking water (Agency For Toxic Substances and Disease Registry, 2005). The exposure to nickel may also occur through skin contact on items or elements that contain nickel. These items or elements may be those that are in the surrounding or those that are actually essential needs. Examples of nickel containing items or substances that human are exposed to are such as shower water, soil, nickel alloyed or plated jewellery, artificial body parts, coins, and stainless steel goods. Unborn child are also prone to be exposed to nickel through the transfer of nickel from their mother’s blood (Agency For Toxic Substances and Disease Registry, 2005). On the other hand, nursing babies may also be exposed to nickel when nickel transfers to the mother’s breast milk. However, the concentration of nickel in breast milk is usually similar or less than that of formula or cow milk.

Nickel is a toxic element that is classified as carcinogenic. There is no safe level concentration recommended in water (Rathor, Chopra and Adhikari, 2014). The absorption of nickel by the human body greatly depends on the nickel metabolism. Assuming that approximately 70% of nickel absorbed would be excreted by the kidney, the other 30% remains in the body. As nickel does not biodegrade, the remaining nickel that stays in the body will affect the activities of cells (Chuah, et al., 2005).

A harmful effect of nickel exposure that is most common is the allergic reaction to nickel (Agency For Toxic Substances and Disease Registry, 2005; Cempel and Nikel, 2006). Approximately 1 to 2 out of 10 people are allergic to nickel. Sensitivity to nickel can occur when a person is in direct or prolonged contact with items or accessories that contains nickel. Once a person is sensitive to nickel, any additional contact with the said element would trigger a reaction.

Workers of the nickel refinery industries are greatly exposed to nickel through inhalation (Rathor, Chopra and Adhikari, 2014). These workers are prone to have significantly higher risk of having chronic sicknesses such as nasal cavity and lung cancer. Not only that, they are also prone to be diagnosed with other types of cancer such as kidney cancer, prostate cancer, and even laryngeal cancer (Rathor, Chopra and Adhikari, 2014). For non-smoking and non-occupational-exposed population, food is a major source of exposure to nickel. Exposure to nickel toxicity would also cause embryo toxic effect, nephrotoxic effect, allergic reaction as well as contact dermatitis (Agency For Toxic Substances and Disease Registry, 2005). However, it was observed in recent studies that the intake of nickel from food is less than 0.2 mg/day.

2.2.3.2 Effect on Plant

For plant, nickel is an essential element at a low concentration (0.05-10mg/kg dry weight) (Rathor, Chopra and Adhikari, 2014). It is commonly absorbed by the soil or culture soil in its ionic form. It was reported that plants absorbs nickel more easily when it is supplied in ionic form instead of chelated form. Rathor, Chopra and Adhikari (2014) reported that an excess in nickel in tomato plants would predominantly damage its root which causes the translocation of all other vital nutrient elements due to the reduction in following absorption.

The absorption of nickel by plants is conditioned by the soil properties including the organic content, as well as the total amount of nickel present in the soil (Hunter and Vergnano, 1952). The amount of exchangeable nickel available affects the accelerated rate of adsorption of nickel by plants (Rathor, Chopra and Adhikari, 2014). At a pH value of soil lower than 5.6, absorption of nickel is favoured. This is because the exchangeable nickel with soil increases with the soil acidity. The addition of lime into an acidic soil would decrease the absorption of nickel by plant while the addition of phosphate content would increase the absorption instead (Crooke and Inkson, 1955). In many plants, a low concentration of nickel is considered as toxic (Rathor, Chopra and Adhikari, 2014). Table 2.2 shows the content of nickel in various plants which would be considered as toxic.

Table 2.2 Content of nickel considered toxic for various plants (Rathor, Chopra and Adhikari, 2014)

Content of Nickel (ppm)	Type of Plant
5	Wheat/ oat
2-60	Buckwheat
15-30	Sugar beet, tomato, potato

When a plant has too high of a nickel concentration, symptoms of toxicity can be observed such as chlorosis, stunted growth of shoot and root, necrosis, deformation of plant parts, as well as spotting. High concentration of nickel would also affect the soil enzyme activity in a negative manner (Kucharski, Boros and Wyszkowska, 2009).

2.3 Nickel Removal Methods

The methods conventionally implemented for the extraction of nickel from aqueous solutions include ion exchange, phytoremediation, chemical precipitation, membrane filtration and electrodialysis (Joshi, 2017).

The ion exchange method is widely used for water treatment. Its working principle is the attraction of soluble ions in liquid phase into a solid phase. A technology usually implemented for the withdrawal of nickel from soil is phytoremediation. This process gives a low-cost solution for soil remediation instead of having to remove and replace the soil. It utilizes plants to transform the contaminants in the soil into non-toxic and hence, it is usually referred to as a green remediation (Joshi, 2017).

Another technique of nickel removal would be the chemical remediation technique. It is the most commonly applied technique especially in polluted areas. This method utilizes insoluble polyacrylate polymer (Rathor, Chopra and Adhikari, 2014). Besides nickel, it is also able to remove other kind of heavy metals including copper and zinc. Chemical precipitation involves coagulants to form precipitation of the heavy metals instead (Joshi, 2017). This method is used by majority of the companies involving nickel plating (Gunatilake, 2015).

Membrane separation is another conventional technology utilized to extract nickel from aqueous solutions. The most generally employed membrane would be the reverse osmosis and ultrafiltration membranes (Kumar, et al., 2017). A pressure driven process that utilizes porous membranes is the ultra-filtration method (Joshi, 2017). Ultrafiltration is used to treat dissolved or colloid nickel compounds by means of low transmembrane pressure. However, this technology produces sludge which is unfavourable (Joshi, 2017). On the other hand, reverse osmosis works in such a way that the semi-permeable membrane only spares clean fluid to infiltrate (Kumar, et al., 2017). It has a high removal efficiency and it is used widely in chemical and environmental water treatment. It is also a common technology used to produce clean drinking water.

Lastly, electrodialysis separates heavy metals by administering electric potential on the ionized species so that they can permeate the ion exchange membrane (Gunatilake, 2015). Although these methods are commonly used methods, there are some inevitable disadvantages to it. The major disadvantages to using conventional technologies are the formation of sludge as well as toxic compounds. Besides that, these methods are costly, time consuming (to remove heavy metals) and gives incomplete removal of some ions (Shamim, 2018).

Another approach to remove nickel is biosorption. The implementation of biosorption is not as widely used in the industry unlike the other methods because it is not as established as other methods. More studies are to be made on the biosorption method to enhance its grounding as a commercial removal method.

2.4 Biosorption

Sorption defines a physio-chemical process whereby a substance attaches to another substance, whereas bio indicates that there is an involvement of a biological entity. Borda and Sparks (2008) describes sorption as any system in which the sorbate and sorbent interacts to result in the accumulation on the sorbate-sorbent interface. Biosorption is represents as the removal of substances from a solution by means of using a biological component (Gadd, 2009). It is a physio-chemical process that is metabolically-independent which is based on a diversity of mechanisms such as absorption, adsorption, ion exchange, precipitation as well as surface complexation (Fomina and Gadd, 2014). Basically, the biosorption process is associated with the removal or sorption of a dissolved or suspended particle (biosorbate) from a liquid phase (solvent) by using a solid phase (biosorbent).

Bioremediation has a large significance such that it provides various benefits such as reduced operating expenditure, minimal disposable sludge ratio volume, immense detoxification efficiency for diluted effluents and in-situ remediation (Shamim, 2018). Each biosorbent has different mechanisms when detoxifying heavy metals or any sort of biosorbates (Park, Yun and Park, 2010). Compared to conventional methods of heavy metal removal, biosorption offers many benefits. According to Shamim (2018), one of the few benefits of biosorption is the economical production of biosorbents. Biosorbents used in the biosorption should be able to be produced at a low cost or for free. Another benefit of biosorption process is that the removal of more than one heavy metal is possible. For an example, green *Cocos Nucifera L.* shell is able to remove chromium, arsenic, and cadmium metals from a solution (Arief, et al., 2008). Besides that, the use of some biosorbents may not require addition of chemical for pre-treatment (Shamim, 2018). Not only that, the biosorption process is an advancement compared to other technologies due to its minimized amount of waste or toxic production (Kumari and Sharma, 2017). Lastly, this heavy removal technique is able to treat large volume of wastewater (Shamim, 2018).

Although it offers many benefits, it also brings several disadvantages such as the reversible biosorption of biosorbates on biosorbents, as well as the overload of metal binding ligand active sites (Abdi and Kazemi, 2015). Traditionally, metals were utilized as biosorbates to remove microbial materials biosorbents from solutions. The earliest biosorption technology was applied in the treatment of waste and sewage (Ullrich, A. H.; Smith, M.W., 1951). Recently, researchers had extended their researches and applications of biosorption for the extraction of organic substances as well as for the restoration of high-valued materials such as protein, drugs, and steroid (Aksu, 2005).

2.4.1 Biosorbates

Biosorbate is defined as the particle or solute to be removed from an aqueous solution by means of biological methods (Fomina and Gadd, 2014). Today, there is a wide range of target biosorbates to be removed and there are also numerous studies that can be found on the biosorption of biosorbates. These biosorbates include metals, colloids, organometalloid, organic as well as inorganic compounds (Fomina and Gadd, 2014). There are many mechanisms that are involved in the removal of various biosorbate and these methods that utilizes biosorbents would clearly be advantageous. Nonetheless, most researches on biosorption were performed on metals and its relevant elements such as radioisotopes, metalloids and actinides (Dhankhar and Hooda, 2011). About 75% of the elements found in the Periodic Table are categorized as metal element and biosorption researches had been done on majority of these elements (Fomina and Gadd, 2014). Most researchers have significant interest on the biosorption of metals on the grounds that the fact that metal toxicity and pollution are currently of great issues.

The important goals of the biosorption researches are usually predefined by the degree of radioactivity, toxicity or the value of the metal of interest. Common goals of researches includes environmental cleaning, recovery as well as the protection of health (Fomina and Gadd, 2014). Few of the most commonly studied metals are lead, mercury, copper, zinc, arsenic, cadmium, nickel, and chromium, along with radionuclides of thorium, uranium and cobalt. These metals may exist in different in different forms with different chemical properties (Kumari and Sharma, 2017; Arief, et al., 2008; Amer, Ahmad and Awwad, 2015). They can be found in its anionic or cationic form, complex form and even at different oxidation states. Generally, common metals in systems are found in its complex or hydroxylated form, subject to the medium pH and composition. However, the form of existence of these metals are usually neglected and assumed to be present in its divalent cation form although inaccurate in many cases (Fomina and Gadd, 2014).

Contrary to metals, organic compounds that are released into the environment would undergo biodegradation with the presence of natural microorganism (Fomina and Gadd, 2014). Its biodegradation potentiality acts as the fundamental principle of established and developing treatment techniques. However, Fomina and Gadd (2014) mentioned that the two main limitations of biodegradation are the hazards of biodegradation products as well as the resistance of xenobiotics to biodegradation. Hence, biosorption was favoured as a promising biotechnology for removing organic compound biosorbates from effluents and waste waters.

In this study, nickel is determined as the biosorbate as it is the solute of interest to be removed from an aqueous solution. The efficiency of removal of nickel by means of biological method will be analysed.

2.4.2 Biosorbents

Dhankhar and Hooda (2011) stated that a biosorbent is any sort of biological material which possess an attraction to pollutants such as heavy metal, organic and inorganic compound. In other words, a biosorbent is a biomaterial which is used to remove biosorbates from a solution. All types of biological materials including microbial (bacteria, fungi, algae, yeast, etc.), animal or plant biomass or waste (hair, sawdust, bark, weeds, cellulose, shoots, etc.) as well as agricultural and food industry waste (fruit or vegetable waste, soybean hull, rice straw or husk, wheat bran, etc.) and other material (chitosan), have underwent investigations and researches in search of a cheap yet very efficient biosorbent (Park, Yun and Park, 2010; Fomina and Gadd, 2014; Shamim, 2018).

The biosorption capacity of most biosorbents were reported and compared among one another in numerous researches. Park, Yun and Park (2010) had reported that some biosorbents can take up to 50% of its dry weight of toxic metals. The biosorption capacity of each biosorbent varies as it primarily depends on the experimental conditions as well as its pre-treatment, if any (Fomina and Gadd, 2014). The experimental data applied by each researcher should be considered whilst comparing the capacity of a biosorbent.

Theoretically, biosorbents used in large scale industries should be economical and readily available. They may originate from industrial waste (or by-products) for free or at a low price, easily grown organisms as well as organisms easily and abundantly accessible from nature (Park, Yun and Park, 2010). A common principle that biosorbents are economically advantageous had inspired the study of biosorption capacity of all sorts of biological materials.

On the other hand, waste acquires transport and treatment costs. If wastes are used as commercial biosorbent, its cost would rise and it would eventually cease to become a waste (Fomina and Gadd, 2014).

A characteristic of biosorbent to be underlined is that the biomass utilized may be either dead or living (Fomina and Gadd, 2014). Dead biomass may be easier to implement due to its less complexity, but its metabolic influence on sorption are usually less satisfactory as compared to living biomass. However, Dhankhar and Hooda (2011) mentioned that it is usually chosen as an alternative in studies of the removal of metal due to several benefits such as its lack of toxicity restraints, and the absence of necessity of nutrients and growth media. Besides that, the uncomplicated absorption and recovery of biosorbates as well as its regenerate-ability and reusability are some of the benefits of dead biosorbents. Last but not least, there is a likelihood of effortless binding of dead cells and the easy modelling of biosorbate uptake of dead cells (Dhankhar and Hooda, 2011).

Living biomasses are capable of degrading organic compounds and are capable of sorption, transporting, complexing as well as transforming biosorbates such as metals, radionuclides and metalloids in addition of other processes that would have contributed to the total removal process. It is applicable for systems that requires metabolic activities as well as when metal removal through pure biosorption is not possible (Malik, 2004).

Table 2.3 below shows the different types of biosorbent utilised to extract different type of heavy metal. It is noticed that many biosorption studies on heavy metal had been done by many researchers. The biosorbent used consist of both living and dead biomass. Meanwhile, Table 2.4 lists down the different studies of biosorption of nickel with the use of different biosorbents. It can be observed that the conditions and nickel removal efficiency differ for each type of biosorbent. This indicates that each biosorbent has its own unique biosorption capability. Hence, it is impossible to standardise a condition for biosorption.

In this study, *Cocos Nucifera L.* shoot is selected as the biosorbent for the study of nickel removal from aqueous solution. This study will analyse the characteristic and efficiency of *Cocos Nucifera L.* shoot as a biosorbent.

Table 2.3 Type of biosorbents studied for different heavy metals (Arief, et al., 2008; Kumari and Sharma, 2017)

Type of Heavy metal	**Type of Biosorbent**
Lead	*Bacillus sp., Micrococus sp., Calotropis procera, Fucus vesiculosus, Rhizopus nigricans, Mucor rouxii*, Lignin, Orange Peel, Palm Kernel Fiber, Rice Husk
Copper	*Stenotropohonas maltophilia, Bacillus cereus, Sargassum sp.* (brown algae), Oocystis, *Pleurotus ostreatus, Aspergillus lentulus, Saccharomyces cerevisiae*, Mango Peel, Rice Bran, Black Gram Husk
Cobalt	*Rhodopseudomonas palustris, Spirogyra hyaline, Saccharomyces cerevisiae, Geotrichum, Penicillium, Rhodococcus opacus,*
Mercury	*Saccharomyces cerevisiae*, *Spirogyra hyaline, Aspergillus flavus, Enterobacter cloacae,* Modified yeast cell
Zinc	*Fucus spiralis*, *Penicillium, Saccharomyces cerevisiae, Streptomyces rimosus*, *Trichoderma,* Rice Bran, Lignin, Palm tree leaves
Chromium	*Micrococcus sp., Bacillus licheniformis, Spirogyra sp., Aspergillus niger*, *Saccharomyces cerevisiae,* Dried activated sludge, Green *Cocos Nucifera L.* shell, Maize bran, olive cake
Cadmium	*Escherichia coli, Fusarium, Ilex paraguaiensis,* Live and Dead *Spirulina, Phanerochaete chrysosporium, Saccharomyces cerevisiae* olive cake, Green *Cocos Nucifera L.* shell powder, Eucalyptus bark,

Table 2.4 Data of different biosorbents for removal of Nickel

Biosorbent/ Type	**Temp. (°C)**	**pH**	**Agitation (rpm)**	**Time (hr)**	**Wt (g/L)**	**Uptake or % removal (mg/g or %)**	**Ref.**
Actinomycetes sp. / Bacteria	30	5	150	24	5	36.55	(Congeevaram, et al., 2007)
Micrococcus sp. / Bacteria	35	5	120	24	-	90	(Sulaymon, Mohammed and Al-Musawi, 2013)
Sargassum sp. /Algae	30	5	150	-	-	26.1	(Subhashini, 2011)
Fucus vesiculosus/ Algae	25	5	-	2	0.25	0.8	(Brinza, Dring and Gavrilescu, 2007)
Ascophyllum nodosum/ Algae	25	6	-	2	0.5-1	50	(Nirmal Kumar and Oommen, 2012)
Aspergillus niger/ Yeast	25	4.5	150	3	1	7.69	(Tay, et al., 2012)
Saccharomyces cerevisiae/ Yeast	25	7	100	2	2	14.1	(Anaemene, 2012)
Pistachio hull waste	25	4-6	-	20min	14	75%	(Zamani Beidokhti, *et al*, 2019)
Palm fiber powder	20	5	-	45min	0.1	4.42	(Boudaoud, et al., 2017)
Acacia leucocephala bark	-	5	-	2	0.7	294.11	(Subbaiah, et al., 2009)

2.4.3 Mechanisms of Biosorption

The mechanism of the biosorption process is quite complex. It can be classified in several ways such as the dependency of metabolism (Shamim, 2018). Other than that, it can also be classified by the position where the process occur such as intracellular accumulation, adsorption at the cell surface or extracellular accumulation (Pieper and Reineke, 2000). Several metal-binding mechanisms participating in the biosorption process are such as ion exchange, precipitation, transportation across the cell membrane, physical adsorption, chelation and complexation.

2.4.3.1 Ion Exchange

Ion exchange is chemical reaction that is reversible whereby an ion of a solution is being exchanged with another ion which with the same charge onto a solid particle which is stagnant (Arief, et al., 2008). This chemical reaction is a reversible reaction. The figure below shows the illustration of ion exchange.

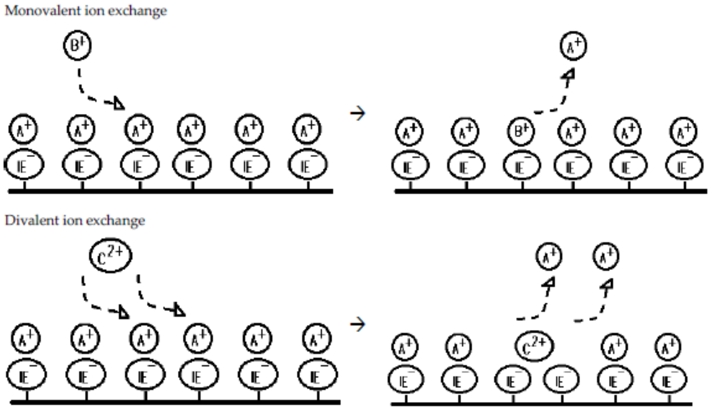


Figure 2.1 Ion Exchange Mechanism (Barros et al., 2016)

Generally, this mechanism is illustrated as (Arief, et al., 2008):

$$M^{X+} + X(HY) \leftrightarrow XH^{+} + MY_{X} \tag{2.1}$$

Whereby

HY - number of acid sites on surface of solid

M^{X+}- metal ion

MY_X - sorbed metal ion

To determine the equilibrium constant of the ion exchange mechanism above,

$$K_{IE}^{H} = \frac{[H^{+}]^{x}[MY_{X}]}{[M^{X+}][HY]^{x}} \qquad (2.2)$$

Polysaccharides are found in the cell wall of an organism in which its ions are exchanged with that of bivalent metal (Pieper and Reineke, 2000).

2.4.3.2 Precipitation

The precipitation mechanism may be dependent or independent of metabolism (Pieper and Reineke, 2000). For metabolism dependent precipitation, it occurs in conjunction with the defence system of an organism whereby a solid is formed in a solution through chemical reaction or inside another solid through diffusion (Shamim, 2018; Pieper and Reineke, 2000). On the other hand, the metabolism independent precipitation occurs as an outcome of the chemical interaction between metal with the surface of cell.

2.4.3.3 Transport across Cell Membrane

According to Pieper and Reineke (2000), the movement of metal from the external to the internal of the cell is usually metabolism dependent as it moves across the cell membrane of an organism. It may be carried out by the same mechanism which transports important ions. The system that transports metal may confuse the heavy metal and important ion with similar charge or ionic radius. The metal will first be bound with the cell wall through independent metabolism before it is being transported into the cell pass the cell membrane (Wang and Chen, 2006).

2.4.3.4 Physical Adsorption

In the case of physical adsorption, weak van der Waals forces of attraction takes place between the biosorbate and surface of biosorbent whereby atoms, molecules or ions are adhered from a liquid, gas, or dissolved solids, onto a surface (Shamim, 2018). Thermodynamically, the physical adsorption happens spontaneously and exothermically (Arief, et al., 2008). In most cases, it does not present as a crucial part in the biosorption process. However, some biosorption process would have physical adsorption as the dominant mechanism such as the adsorption of cadmium by olive cake (Al-Anber and Matouq, 2008). At the surface of the biosorbent, the adsorption process forms a film of biosorbate. This mechanism is either classified as either physi-sorption or chemi-sorption, due to the weak van der Waals forces of attraction or the covalent bonding, respectively, between biosorbent-biosorbate and biosorbate-biosorbate (Shamim, 2018).

2.4.3.5 Chelation

Chelation is a distinct method of binding ions or molecules which includes two or more distinct coordinate bonds which are present or formed between a single central atom and a polydentate ligand (Shamim, 2018). According to Arief *et al.*, it is described as a binding between a metal ion and an organic molecule which serves as a ligand, into a ring structure.

2.4.3.6 Complexation

The complexation mechanism mainly involves interaction between the metal cation and ligand of cell wall which forms a complex that precipitates on the cell wall (Arief, et al., 2008). According to Abdi and Kazemi (2015), the number of proton discharged into the solution decline by order of $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+} > Mg^{2+}$ due to the capability of metal to compete with other protons for vacant organic binding sites.

2.4.4 Factors Affecting Biosorption

Besides the type of sorbate and its chemical form, there are several physical and chemical factors that controls the performance of the overall biosorption process (Fomina and Gadd, 2014; Park, Yun and Park, 2010). These factors were included in the following sub-sections.

2.4.4.1 pH of solution

The pH of a solution seems to be the ultimate vital factor which regulates the biosorption process. It is capable of affecting the chemistry of the pollutant solution, the activity of the biosorbents' functional group, as well as its competition with other ions that coexists in the solution (Vijayaraghavan and Yun, 2008). A rise in pH value would boost the removal of basic dyes or cationic metals but weakens that of acidic dyes or anionic metals.

2.4.4.2 Temperature

It appeared that the temperature of the solution affects the biosorption at a lower degree when the temperature is between 25°C to 35°C. A higher temperature usually improves the removal of biosorbates through biosorption as it increases the kinetic energy as well as its surface activity. This is because the removal of most biosorbates through biosorption as endothermic. However, an elevated temperature would also bring destruction to the physical feature of the biosorbent (Park, Yun and Park, 2010).

2.4.4.3 Nature of biosorbents

The nature of the biosorbent includes the physical and chemical properties and modification, binding site availability, dosage, prehistory treatment and growth as well as its size are crucial factors that contributes to the performance of a biosorption process (Fomina and Gadd, 2014). Increasing the dosage of the biosorbent would boost the removal efficiency but cause a drop in the quantity of biosorbed biosorbate for a unit weight of biosorbent. On the other hand, a decrease in biosorbent size would be preferable for batch processes as there would be a higher surface area. However, smaller particles would cause clogging to column processes.

2.4.4.4 Initial biosorbate concentration

Increasing the initial biosorbate concentration would give an opposite result as compared to that of increasing the biosorbent dosage. It causes a drop in the removal efficiency but increases the quantity of absorbed biosorbate for every unit weight of biosorbent. However, its effect on the removal efficiency is not as prominent.

2.4.4.5 Agitation speed

The faster the speed of agitation, the better the rate of removal of biosorbate. This is because of the minimized resistance to mass transfer. Nonetheless, it may inflict damage to the biosorbent’s physical form.

2.4.4.6 Ionic strength of solution

The inhibitory impact of the ionic strength is required to be investigated because it influences the removal of biosorbent through biosorption as it competes with the biosorbates for active sites. A rise in ionic strength results in the reduction in the removal of biosorbents through biosorption as it competes for binding sites with the active sites.

2.4.4.7 Contact time

As the contact time increases, there may be more opportunity for biosorbate to be attached on the active sites. However, any extra time more than the optimum contact time will be considered redundant as biosorption may not occur anymore or desorption may occur which reduces the efficiency.

2.4.4.8 Other pollutant effects

A higher concentration of other pollutant would result in the effect of other pollutants towards the biosorption of the interested pollutant. These pollutants would compete for binding sites or create complexes with the binding sites. Then, the biosorption of biosorbate would decrease as the number of available active sites would be less.

2.4.5 Isotherm Models

The equilibrium data of metal biosorption correlates to the adsorption isotherm. The adsorption isotherm is an indication of the arrangement of adsorbed molecules between both solid and fluid phase at equilibrium, whereby it describes the relation between adsorbed solute and concentration of solute in liquid or gas phase, based on several assumptions (Zamani Beidokhti, (Omid) Naeeni and AbdiGhahroudi, 2019; Chandra Joshi, 2017; Ponnusamy, 2010). These isotherms are utilized in the determination of type of biosorption that takes place and to identify the maximum equilibrium adsorption of a biosorbent (Zamani Beidokhti, (Omid) Naeeni and AbdiGhahroudi, 2019).

In pursuance of understanding the adsorption characteristics of *Cocos. Nucifera L.* shoot as a low-cost biosorbent, experimental data obtained as a result of batch adsorption will be evaluated using two common adsorption isotherms: Langmuir and Freundlich isotherms. From the graphs plotted for

Langmuir and Freundlich, the correlation coefficient, R^2 for each isotherm will identify the suitability of the isotherm to the biosorption process.

2.4.5.1 Langmuir Isotherm

The Langmuir isotherm was published by Langmuir in 1918 with accordance to an assumption whereby the maximum adsorption is achieved when the monolayer of solute on adsorbent surface becomes saturated (Guyo, et al., 2016; Ponnusamy, 2010; Sujatha, Kalarani and Kumar, 2013). It is further assumed that the adsorption energy is constant (Guyo, et al., 2016).

The Langmuir isotherm is illustrated the equation (Zamani Beidokhti, (Omid) Naeeni and AbdiGhahroudi, 2019):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2.3}$$

Where

q_e- amount of metal ions biosorbed at equilibrium (mg/g)

C_e – equilibrium concentration of metal ions (mg/L)

q_m –maximum biosorption capacity (mg/g)

K_L- Langmuir equilibrium constant

The Langmuir isotherm is further linearized to form:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \tag{2.4}$$

The Separation factor of the Langmuir Isotherm is expressed as (Guyo, et al., 2016):

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

Where

C_m- initial concentration of metal ions (mg/L)

R_L value calculated symbolizes to favourability an isotherm to the biosorption process. The isotherm is deemed as favourable if $0<R_L<1$ or R_L equals to 0. However, it is said to be unfavourable if the R_L value exceeds 1. A linear graph of c_e/q_e vs c_e will be plotted to obtain K_L for the calculation of R_L, as well as the correlation coefficient, R^2.

2.4.5.2 Freundlich Isotherm

The Freundlich Isotherm was published by Freundlich and Kuster (1907) as a non-linear sorption model (Shamim, 2018). The isotherm is established with the assumption that there adsorption on different sites with distinctive adsorption energies or in other words, a heterogenous adsorption(Ponnusamy, 2010). The Freundlich isotherm is given by:

$$q_e = K_f C_e{}^{1/n} \tag{2.6}$$

Where

q_e – amount of metal ion removed (mg/g)

C_e – concentration of metal ion at equilibrium (mg/L)

K_f – adsorption capacity (Freundlich constant)

n –Freundlich constant

Freundlich isotherm equation can be linearized into:

$$\ln q_e = \ln K_f - \frac{1}{n} \ln C_e \tag{2.7}$$

When n value is more than 1, the adsorption that takes place is a physical process. The adsorption is a chemical process if n is less than 1. If the n equals to 1, the adsorption is linear. A linear graph of $\ln q_e$ vs $\ln c_e$ will be plotted to determine K_f and n, as well as the correlation coefficient, R^2.

2.4.6 Kinetic Models

Adsorption is defined as a process whereby a particle or solute attaches on the adsorbent surface. Adsorption kinetics describes the retention or release of solute from liquid to solid at given conditions, using a line or curve (Kajjumba, et al., 2016). Physical and chemical processes take place during adsorption; physisorption and chemisorption (Kajjumba, et al., 2016). According to Kajjumba, et al. (2016), physisorption occurs through weak van der Waals forces while chemisorption takes place due to the strong bonds formed between the biosorbent and biosorbate through the transfer of electrons. In this study, the kinetic models are practiced to investigate the mechanism of the biosorption of nickel by *Cocos Nucifera L.* shoot. The biosorption kinetics to be analysed in this study are the Pseudo first-order model and Pseudo second-order model.

2.4.6.1 Pseudo First-Order Model

Pseudo first-order model, also known as Lagergren model, outlines the adsorption with first order mechanism. The Lagergren model rate equation is shown as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.8}$$

Where

q_e – amount biosorbent adsorbed at equilibrium (mg/g)

q_t – amount biosorbent adsorbed at time t (mg/g)

k_1 – rate constant

Integrating the equation gives:

$$log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2.9}$$

A linear graph of $log(q_e - q_t)$ versus time will be plotted to identify the rate constant and correlation coefficient, R^2.

2.4.6.2 Pseudo Second-Order Model

It is assumed for the Pseudo Second-Order Model that the adsorbate adsorption rate corresponds to the vacant active sites on the surface of adsorbent (Kajjumba, et al., 2016). The Pseudo Second-Order Model is expressed through an equation below:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2.10}$$

Where

q_e – amount biosorbent adsorbed at equilibrium (mg/g)

q_t – amount biosorbent adsorbed at time t (mg/g)

k_2 – rate constant

The linear form of the equation is:

$$\frac{1}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e}t \tag{2.11}$$

It is suggested in the pseudo-second-order rate expression that chemical process may control the adsorption process (Boudaoud, et al., 2017). Boudaoud, et al. (2017) mentioned that the chemical process involves covalent forces which is the sharing or exchange of electrons among the biosorbent and biosorbate.
A linear graph of $1/q_t$ versus time will be plotted to figure out the rate constant and correlation coefficient, R^2.

2.5 *Cocos Nucifera L.* Shoot

Cocos. nucifera L. is commonly known by laymen as the coconut fruit tree. It is a distinguished member of the *Arecaceae* (palm) family, and the Cocoideae subfamily (Perera, 2015). In different regions of the world, the fruit has its own local name in different languages such as *kelapa*/*nyior* (Malaysia/ Indonesia), *niyog* (Philippines), *niu* (Polynesia), *kokospalme* (German) and etcetera. The Polynesian local name of the *Cocos Nucifera L.* fruit (*niu*) is a derivative from the Malay word (*nyior*) which it referred to as a proof that the fruit tree originates from the Malay-Indonesian region (Chan and Elevitch, 2006).

The coconut fruit plant can be found all around the world as it is the utmost widespread fruit on the Earth(Lima, et al., 2015). The fruit plant is prominently seen mainly in coastal areas in tropical and subtropical regions at 20-23° North and South of the equator (Chan and Elevitch, 2006). It can also be found outside of these latitudes. However, those that are found outside the latitude will flower but its fruits are not able to develop as usual. It is believed that the fruit plant originates from Southeast Asian countries including the Philippines, Malaysia, and Indonesia, as well as Melanesia (Lima, et al., 2015; Chan and Elevitch, 2006). The fruit plant was speculated to have been brought to India followed by East Africa through Malay and Arabian traders around 3000 years ago. In the 16th century, European explorers then introduced the fruit plant into West Africa whereby it was then distributed throughout the continents of America as well as other tropical countries. it was also believed that the coconuts in the Pacific were brought in by migrating Polynesians about 4500 years ago (Chan and Elevitch, 2006). Currently, the fruit tree can be found far and wide in the tropics as it has been interlaced into the lives of the residents.

The *Cocos Nucifera L.* tree consists of a brown greyish trunk topped with a crown of leaves. Unlike other type of fruit tree, its trunk does not branch out. The *Cocos Nucifera L.* root system is fasciculated whereby it grows in a bunch (Lima, et al., 2015). The physical properties of the soil as well as the water table depth affects the depth of the *Cocos Nucifera L.* tree’s rooting. The top of the tree consist the fruits attached to the tree by its stalk, pinnate leaves and inflorescence (Chan and Elevitch, 2006). As the plant is monoecious, it consists of both male and female reproductive organs on a plant itself.

On islands in the Pacific where there are close to no natural land resources, the coconut plays a vital part in supplying majority of the necessities for survival such as food and beverage, mats, utensils, fibre, and even medicine (Chan and Elevitch, 2006). Matured kernels are eaten as food, shredded kernels are found in sweets and desserts, and the milk extracted from the kernel are used in curries, other aromatic food, as well as desserts (Perera, 2015). Besides that, coconut oil is used for cooking and even for beauty purposes. The coconut water and kernel found in premature coconut fruits are eaten and drank as refreshments. The table below shows the examples of different uses of various parts of the *Cocos Nucifera L.* tree itself.

In Figure 2.2, the *Cocos Nucifera L.* shoot is pointed out with a red arrow. The *Cocos Nucifera L.* shoot holds the *Cocos Nucifera L.* fruit to the tree and is often separated of with fruit when harvesting the fruit. Unlike the other parts of the coconut tree, the *Cocos Nucifera L.* shoot is usually thrown away. Besides being able to remove of reduce the nickel pollution at a low cost, this *Cocos Nucifera L.* shoot as a biosorbent can also reduce the agriculture waste by reusing it rather than just disposing it off. The *Cocos Nucifera L.* shoot can be collected from *Cocos Nucifera L.* fruit drink vendors or restaurants at a large quantity for free as it would be thrown away in the end. In this study, the *Cocos Nucifera L.* shoot will be prepared into dried powder form. Its physical characteristics and efficiency in removing nickel will be studied. Besides, many researchers have studied other types of biomass as biosorbent and *Cocos Nucifera L.* shoot is not one of them. Hence, this study could be a starting point to turn the *Cocos Nucifera L.* waste into something useful in the industry to the environment.

Figure 2.2 *Cocos Nucifera L.* Fruit Shoot (Grant A., 2018)

CHAPTER 3

METHODOLOGY

3.1 Flowchart

The main aim of this study was to examine the performance and suitability of the *Cocos Nucifera L.* shoot as a biosorbent in the removal of nickel from aqueous solution. The whole study was divided into 4 parts which included performing literature review, material preparations, characterisation of biosorbent, and experimental test. Figure 3.1 below presents a flowchart of the work.

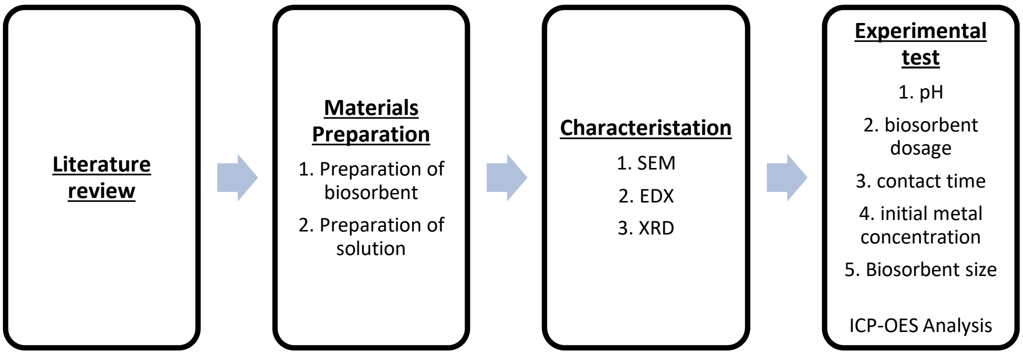


Figure 3.1 Flowchart of Work

In this chapter, the preparation of *Cocos Nucifera L.* shoot as biosorbent as well as nickel stock solution were discussed. The characterisation of the *Cocos Nucifera L.* shoot included several equipment such as the scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX) as well as X-ray diffraction (XRD). Then, the experimental procedures in which the efficiency of *Cocos Nucifera L.* shoot as biosorbent of nickel were tested on several parameters.

3.2 Preparation of Material

3.2.1 Preparation of *Cocos Nucifera L.* Shoot Powder

The *Cocos Nucifera L.* shoots were collected from fresh *Cocos Nucifera L.* drink vendors in the area of Jalan Manis, as well as in the morning market of Bandar Sungai Long. First of all, the collected *Cocos Nucifera L.* shoots were washed thoroughly and rinsed multiple times with deionised water to get rid of any dust or dirt particle. Secondly, the washed *Cocos Nucifera L.* shoots were oven dried for approximately 7 to 8 hours at a temperature of 80℃. To ensure that the *Cocos Nucifera L.* shoots were totally dry, the weight of *Cocos Nucifera L.* shoots were measure at interval until it reached a constant weight. After drying, the *Cocos Nucifera L.* shoots were grinded and then sieved into 3 different size range which are 300 to 850 µm, 850 µm to 1 mm, and 1 mm to 2 mm. Figure 3.1 shows the *Cocos Nucifera L.* shoots after it has been washed and dried in the oven whereas Figure 3.2 shows the grinded dried *Cocos Nucifera L.* shoots.

Figure 3.2 Dried *Cocos Nucifera L.* shoots

Figure 3.3 Grinded dried *Cocos Nucifera L.* shoots

Lastly, the sieved *Cocos Nucifera L.* shoots were stored in clean airtight container in order to prevent moisture from entering. Figure 3.4 shows the sieves used to separate the biosorbent powder by size whereas Figure 3.5 shows the grinded *Cocos Nucifera L.* shoots being sieved. Figure 3.6 shows the powders of different sized stored in different storage bottle. Powder of sizes below 300 μm and above 2 mm were stored separately in Ziplock bags.

Figure 3.4 Sieves used for separation of size

Figure 3.5 Sieving of grinded dried *Cocos Nucifera L.* shoots

Figure 3.6 Stored *Cocos Nucifera L.* shoot powder

3.2.2 Preparation of Solutions

Nickel (II) nitrate solids were used to prepare the nickel stock solution. To the extent of preparing nickel stock solution with desired concentration of 100 mg/L, 0.156 g of nickel (II) nitrate was required to be dissolved in 1 litre of deionised water. Deionised water was utilized for the dilution stock solution concentration during the experimental test.

0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) were used as acid and base to manipulate the pH of the stock solution. In order to prepare 0.1 M HCl solution, 8.3 ml of 37 % concentrated HCl was added into 1 litre of deionised water. On the other hand, 0.1 M NaOH solution was prepared by dissolving 4 g of NaOH pellets into 1 litre of deionised water. These solutions were stored properly in a glass storage bottle and placed in a safe place.

3.3 Characterisation of Biosorbent

The characterisation of the *Cocos Nucifera L.* shoot was essential in the interest of studying the biosorption mechanism of the *Cocos Nucifera L.* shoot as well as the suitability of *Cocos Nucifera L.* shoot as a biosorbent for nickel. Several equipment was used to analyse the surface morphology, surface functional group available, as well as the elemental composition of the *Cocos Nucifera L.* shoot. Scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX) as well as x-ray diffraction spectroscopy (XRD) were used for the characterisation of biosorbent.

3.3.1 SEM Analysis

The SEM was used in this study to scan and observe the surface structure of the *Cocos Nucifera L.* shoot which may be responsible for the biosorption of nickel. Figure 3.7 shows the Hitachi S-3400N Scanning Electron Microscope (SEM) model available in UTAR. The *Cocos Nucifera L.* shoots before and after biosorption were prepared by drying to a constant weight. Before analysis, small amount of samples were spread into a thin layer on the sample holder, before being coated with gold-platinum coating. The coated samples were then placed into the sample chamber of the SEM machine. The samples were scanned at magnifications of 300x, 700x, 800x and 1500x. Magnified image of the samples were saved and compared.

Figure 3.7 Scanning Electron Microscope (Hitachi S-3400N model)

3.3.2 EDX Analysis

EDX was used in conjunction with the scanning electron microscope (SEM). In this study, EDX was utilized to identify the presence and composition of certain elements on the biosorbent surface. The results obtained from the EDX analysis were compared.

3.3.3 XRD Analysis

XRD was used to observe the atom distribution in the lattice of the Cocos Nucifera L. shoot before and after biosorption. The XRD-600 SHIMADZU model was used to carry out the XRD analysis for this study.

The *Cocos Nucifera L.* shoot before and after biosorption were dried and grinded into powder for the XRD analysis. The dried sample powders were placed in the provided sample holder. The samples were ensured compact, smooth and held firmly in the sample holder to make sure that it does not fall out during the scan. Figure 3.8 shows the grounded *Cocos Nucifera L.* shoot using mortar and pestle whereas Figure 3.9 shows the prepared sample powder for XRD analysis.

The type of radiation used in this analysis was the Cu-K alpha radiation. The samples were scanned continuously at the rate of 2°/min within the diffraction angle (2ϴ) ranging from 5° to 70°.

Figure 3.8 Grinded *Cocos Nucifera L.* shoot

Figure 3.9 Sample for XRD analysis

3.4 Experimental Setup

The biosorption experiment were conducted using 250 mL conical flasks and incubation shaker. As there were several parameters that were investigated for this study, each parameter had its own set of setup and study. After each experiment has been conducted, the *Cocos Nucifera L.* shoot biosorbents were filtered out from the solution by means of a filter paper, and the final nickel concentration will be obtained by utilizing an inductively coupled plasma-optical emission spectrometry (ICP-OES). The Figure 3.10 below shows the general steps of the batch experiment.

Upon obtaining the results from the ICP-OES analysis, the percentage removal of individual sample was calculated and studied. The calculated removal percentages were used to observe and analyse the trend of removal for each parameter.

To calculate the amount of biosorbate uptake at equilibrium:

$$qe = \frac{CoVo - CeVe}{M} \tag{3.1}$$

Where

q_e – metal uptake capacity (mg/g)

C_0/C_e – initial / equilibrium metal concentration (mg/L)

V_0/V_e – initial / equilibrium volume of stock solution (L)

M – dry mass of biosorbate added (g)

To calculate the percentage removal of nickel:

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \tag{3.2}$$

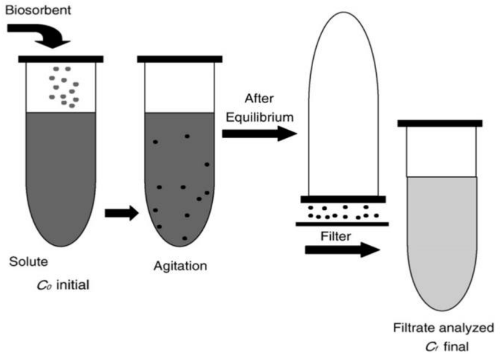


Figure 3.10 General Procedure of Batch Experiment

3.4.1 pH

For this parameter, the pH of the nickel stock solutions was manipulated from 2, 3, 6, 7, 9 to 11. A pH meter was utilised to measure the pH value of each stock solution. 0.1 M HCl and 0.1 M NaOH were added into 100 mL of nickel stock solution to manipulate the pH value. 5.0 g of biosorbent was added into the prepared stock solutions and stirred at a constant speed of 100 rpm for 20 minutes at room temperature. The nickel solutions after biosorption were filtered out and stored in centrifuge tubes. A total 6 data were collected and the pH with the optimum adsorption of nickel determined by ICP-OES test.

3.4.2 Biosorbent dosage

To study this parameter, the absorbent dosage was manipulated with an increment of 5 g from 5 g to 30 g. The biosorbent with different dosage were added into 100 mL of nickel stock solution with the concentration of 100 mg/L at a fixed pH 7 and stirred at a constant speed of 100 rpm for 20 minutes at room temperature. A set of 6 data were obtained after carrying out the experiment by testing the filtered nickel solution through ICP-OES.

3.4.3 Contact time

The allocated amount of time was manipulated by an increment of 5 minutes from a range of 10 minutes to 35 minutes. 5 g of biosorbent was added into 100mL of stock solution at a fixed pH of 7 with the concentration of 100mg/L and stirred at a constant speed of 100 rpm at room temperature. After that, the biosorbent and nickel solutions were separated by means of filtration and the nickel solution were stored in centrifuge tubes for analysis.

3.4.4 Initial metal concentration

The initial metal concentration of the nickel stock solution was manipulated with a decrement of 20 mg/L for each round, within a range of 100 mg/L to 20 mg/L by means of dilution with deionised water. After dilution, a volume of 100 mL of the diluted solutions were used. 5 g biosorbent dosage was added into 100 mL of stock solution (with 100 mg/L nickel concentration) at pH 7., Then, the mixture was stirred at a constant speed of 100 rpm at room temperature for 20 minutes. A set of 6 data were obtained and analysed to analyse the effectiveness of the removal of nickel ion at different initial nickel concentration.

3.4.5 Biosorbent size

The size of biosorbent was manipulated in 300 to 850 μm, 850 μm to 1 mm, and 1 mm to 2 mm. For each biosorbent size, 5 g was added into 100 mL of stock solution of pH 7 and 100 mg/L of nickel concentration in 3 different flasks, followed by stirring at a constant speed of 100 rpm for 20 minutes at room temperature. A set of 3 data were obtained and analysed to examine the performance of the nickel ion removal of at different sizes.

3.4.6 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) Analysis

The ICP-OES was utilized in this study to observe and analyse the nickel composition of the nickel solution after biosorption. The concentration of nickel in each sample were obtained and the percentage removal of nickel for each parameter were analysed. For this analysis, the collected nickel solutions after biosorption were placed in 15 ml centrifuge tubes. Stock solutions with nickel concentrations of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L as well as deionised water were filled in individual 50 mL centrifuge tubes for calibration. The prepared samples and solutions were placed accordingly into the provided tray and the analysis was carried out.

Figure 3.11 shows a set of samples after the biosorption process before filter while Figure 3.12 shows the separation process of biosorbent and nickel solution by means of filtration using filter paper. Figure 3.13 shows the filtered nickel solution stored in medium sized centrifugal tubes before it is being transferred into smaller centrifugal tubes for ICP-OES analysis.

Figure 3.11 Set of samples after biosorption

Figure 3.12 Filtration process of nickel solution

Figure 3.13 Storage of filtered nickel solution

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Parameter Effect Study

4.1.1 Effect of pH

The pH of a solution played a vital role as it greatly affected the performance of heavy metal ions biosorption (Arief, et al., 2008). It was due to the significant impact on the biosorbent surface charge, extent of ionization as well as the biosorbent's speciation caused by the pH values of a solution. Figure 4.1 showed the percentage removal of nickel from aqueous solution with pH as the variable parameter at values pH 2, pH 4, pH 6, pH 7, pH 9, and pH 11.

Based on Figure 4.1 it can be observed that extreme pH values such as pH 2 and pH 11 possessed the lowest removal of nickel of 59.72 % and 57.66 %, respectively, as compared to other pH values. Low nickel removal at very low pH can be interpreted by the excess amount of H^+ ions dissociated from HCl which competed with nickel for the active sites available in the biosorbents (Khan Academy, n.d.). However, Boudaoud, et al. (2017) stated that high concentration of protons at low pH caused metal binding sites to be positively charged which caused it to repel Ni(II) cations. Meanwhile, at higher pH value conditions, precipitation was observed. This may be explained by the hydroxide formation of nickel with OH^- ions present in alkali condition (Subbaiah, et al., 2009). Formation of nickel precipitate decreased the biosorption of nickel and hence, the low percentage removal of nickel at high pH.

Less extreme pH gave better percentage of removal of more than 70 %. At neutral pH (pH 7), the percentage of removal was at 74.07 % which was higher than the percentage of nickel removal at extreme pH values. However, the removal of nickel through biosorption was the highest at pH 9 with 82.55 % removal of nickel. Abdi and Kazemi (2015) stated that the biosorption capability was less desired at low pH values and that it increased with increasing pH until it reached the optimum pH value. From Figure 4.1, it is observed that the nickel removal percentage did increase with pH, although not as consistent as desired. Upon reaching the optimum pH (pH 9), the nickel removal dropped drastically with further increase of pH value.

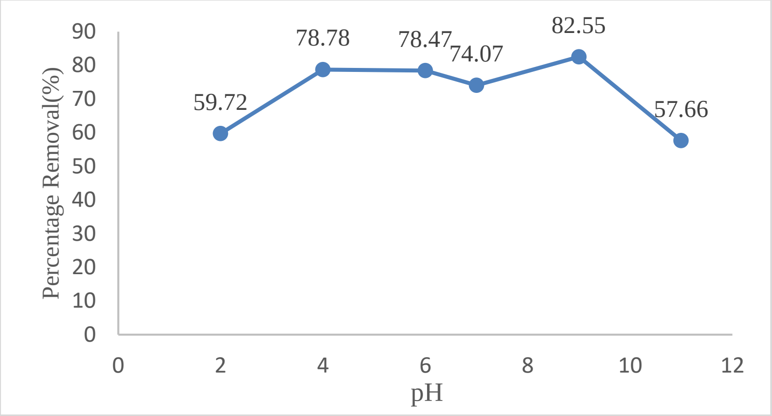


Figure 4.1 Percentage Removal of Nickel for pH Parameter

4.1.2 Effect of Biosorbent Dosage

Although the biosorption capacity increased with the amount of biosorbent added, it was important to determine the maximum biosorption capacity for a certain concentration to prevent overdose or wastage of biosorbent (Guyo, et al., 2016). Figure 4.2 showed the impact of different biosorbent dosage on the percentage removal of nickel from aqueous solution.

It can be observed from Figure 4.2 that a rise in biosorbent dosage produces a surge in the quantity of nickel removed from the solution. As the biosorbent dosage increased from 5 to 15 g, there was a steady rise in the removal percentage of nickel from 78.13 % to 86.05 %. This was by reason of the increment of surface area and vacant active sites when the dosage increased (Zamani Beidokhti, (Omid) Naeeni and AbdiGhahroudi, 2019). A larger increase in nickel removal percentage was observed at 25 g of biosorbent dosage with 89.56 % removal. After 25 g, the increment in removal percentage of nickel decelerates, showing that the rise in adsorbent dosage caused insignificant increased in nickel removal. This proposed that the equilibrium between both biosorbent and biosorbate may have been reached at this point (Zamani Beidokhti, (Omid) Naeeni and AbdiGhahroudi, 2019). Thus, the optimum biosorbent dosage was 25 g.

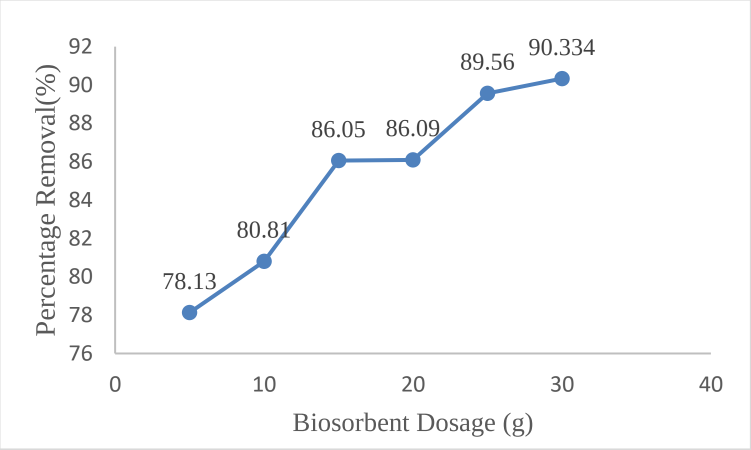


Figure 4.2 Percentage removal of Nickel for Biosorbent Dosage Parameter

4.1.3 Contact Time

Figure 4.3 represented a graph of the percentage removal of nickel with respect to the contact time (agitation time) of biosorbent and biosorbate. Figure 4.3 showed a slight increase of percentage removal of nickel from aqueous solution from 76.31 % to 81.59 % when the agitation time increased from 10 to 20 minutes. At 25 minutes, a sudden drop of percentage removal to 70.35 % was observed. However, the percentage removal of nickel increased again at 30 minutes, to 87.91 %, and remained almost constant at 35 minutes. This showed that the adsorption rate of nickel increased in initial stages. This may be interpreted by the largely vacant active sites for adsorption (Guyo, et al., 2016).

Upon reaching equilibrium at 30 minutes, the adsorption rate remained approximately constant. At equilibrium, most active sites are filled and exhausted, causing a drop in adsorption rate which explained the constant percentage removal of nickel after 30 minutes of agitation time (Guyo, et al., 2016). Hence, 30 minutes was the chosen optimum agitation time for biosorption of nickel by *Cocos Nucifera L*. shoot.

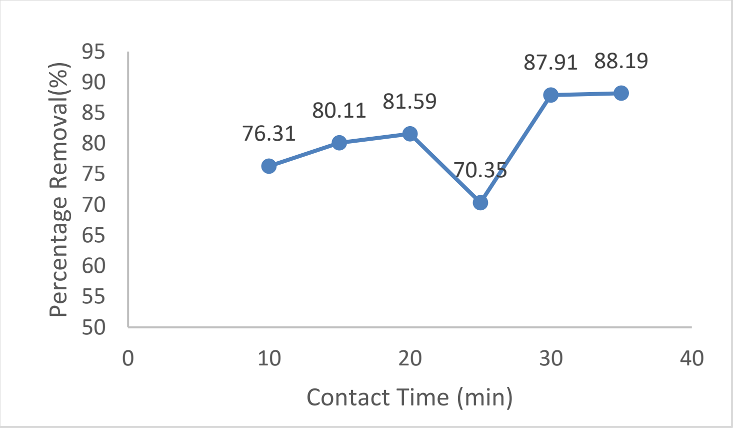


Figure 4.3 Percentage removal of Nickel for Contact Time Parameter

4.1.4 Effect of Initial Metal Concentration

Figure 4.4 showed the impact of initial concentration on the removal of nickel through biosorption with constant biosorbent dosage. It was noticed from Figure 4.4 that the initial concentration of nickel in aqueous solution gave insignificant effect on the removal percentage. Initial concentration of 20 mg/L seemed to have slightly higher removal percentage of nickel compared to 100 mg/L. This might be resulted from the inadequacy of competition for active sites for initial concentration of 20 mg/L as compared to 100 mg/L (Chuah, et al., 2005). However, the increase of removal percentage was not that significant such that the change in initial metal concentration does not result in big difference on the removal percentage. Thus, it can be deduced that the initial concentration of biosorbate did not affect the biosorption process.

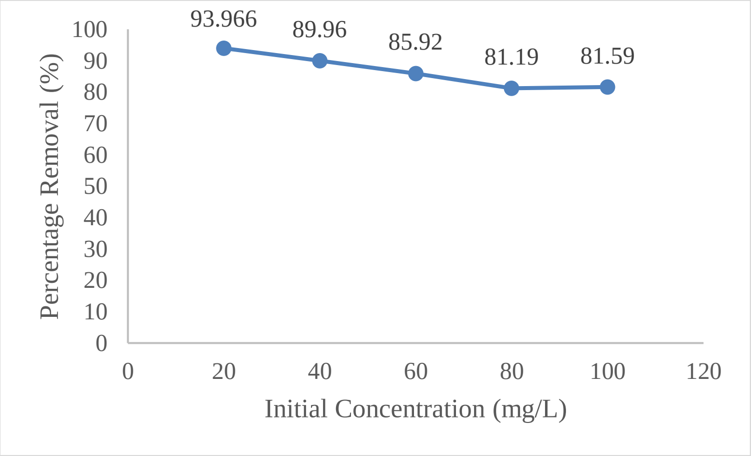


Figure 4.4 Percentage removal of Nickel for Initial Metal Concentration Parameter

4.1.5 Effect of Biosorbent Size

Figure 4.5 showed the impact of biosorbent size on the extraction of nickel. Referring to bar graph shown in Figure 4.5, biosorbent within 850 to 1000 µm (1 mm) size range yielded the lowest removal percentage of nickel from aqueous solution at 86.74 % followed by 1 to 2 mm sized biosorbents with 88.62 % nickel removal. Biosorbent sized 300 to 850 µm were able to remove the largest quantity of nickel from aqueous solution by 90.87 %. It was expected that the percentage of nickel removed decreased when the size of particle increased due to the decrease in surface area. However, it was observed in the Figure 4.5 that the biosorbent with particle size ranged 1000 to 2000 µm resulted greater removal percentage than 850 to 1000 µm. This might be explained by the increase of number of micropores as the particle size increased (Charles.I and Odoemelam, 2010). Charles.I and Odoemelam (2010) also stated that the increment in percentage removal was due to the rise in the quantity of vacant active sites with the increase in micropores.

Although biosorbents with the size of 1000 to 2000 µm resulted higher nickel removal compared to 850 to 1000 µm, biosorbent with the size of 300 to 850 µm showed the highest nickel removal. Particles of smaller size gave larger surface area that offered higher exposure of vacant active sites (Chuah, et al., 2005). As adsorption occurred on the surface, smaller particle size with larger surface area gave better adsorption. Hence, biosorbent with 300 to 850µm size was the optimum particle size.

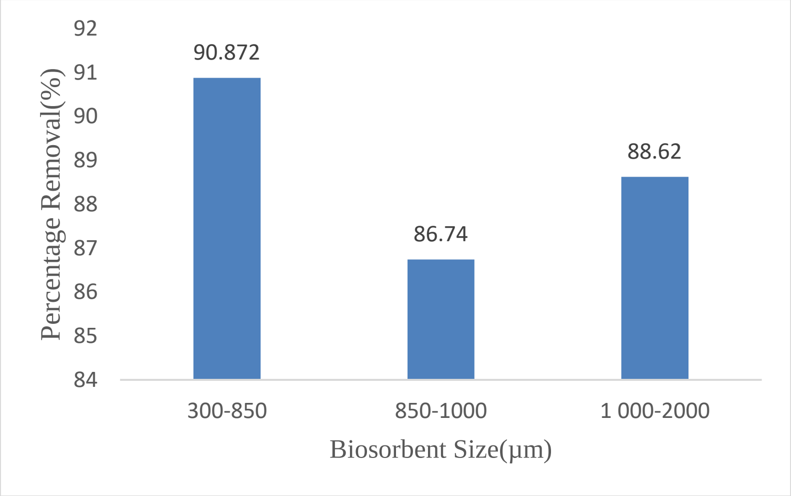


Figure 4.5 Percentage removal of Nickel for Biosorbent Size Parameter

The obtained optimum parameters for the removal of nickel by *Cocos Nucifera* L. shoot were tabulated in Table 4.1.

Table 4.1 Optimum Condition of Nickel Removal by *Cocos Nucifera* L. Shoot

Parameter	**Optimum**
pH	9
Biosorbent Dosage (g)	25
Contact Time (min)	30
Biosorbent size (µm)	300-850

4.2 Biosorption Isotherm

To analyse the biosorption character of *Cocos Nucifera L.* shoot, the Langmuir and Freundlich isotherm model were applied. These models described the distribution of solute through adsorption between liquid and solid phase (Pino, et al., 2006; Joshi, 2018). The data collected from the batch experiment carried out were used to plot linear graphs for Langmuir (Ce/Qe vs Ce) and Freundlich (log Qe vs log Ce) isotherm. Figure 4.6 showed the linear plot for Langmuir isotherm model whereas Figure 4.7 showed the linear plot for Freundlich isotherm. The correlation coefficient (R^2) represents suitability of the isotherm to the biosorption nature of *Cocos Nucifera L.* shoot.

In accordance to Figure 4.6, it was discovered that the graph produced a nearly perfect linear line with correlation coefficient, R^2 of 0.9955. From the linear equation obtained in Figure 4.6, the calculated q_{max} and K_L are 0.74912 mg/g and 0.36809 L/mg, respectively. The calculated R_L was 0.026. According to Ayawei, Ebelegi and Wankasi (2017), the adsorption process was favourable as it was within the range of $0< R_L <L$. On the other hand, Figure 4.7 showed a less linear line with a correlation coefficient, R^2 of 0.9158, for Freundlich isotherm. Using the linear equation shown in figure 4.7, K_f that represented the adsorption capacity was calculated to be 10.0463 whereas n which corresponds to the intensity of adsorption was calculated at -0.2310.

By comparing the correlation coefficient of both the Langmuir and Freundlich isotherm model, which were 0.9955 and 0.9158, respectively, it was observed that Langmuir isotherm has a greater correlation coefficient which is closer to 1. As the correlation coefficient represent the suitability of isotherm, it can be deduced that the Langmuir isotherm best described the biosorption nature of the *Cocos Nucifera L.* shoot. Hence, the *Cocos Nucifera L.* shoot exhibited monolayer adsorption on its surface. When the active sites on the surface are no longer vacant in which the surface was saturated with nickel, maximum adsorption was achieved (Desta, 2013).

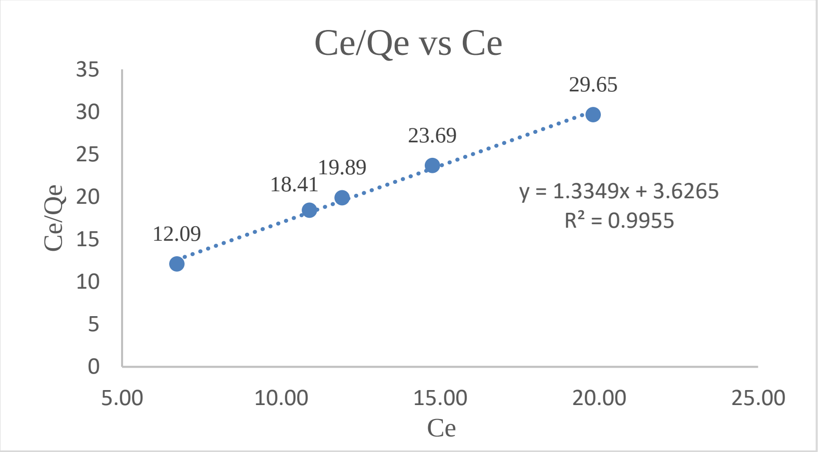


Figure 4.6 Graph of Ce/Qe vs Ce for Langmuir Isotherm

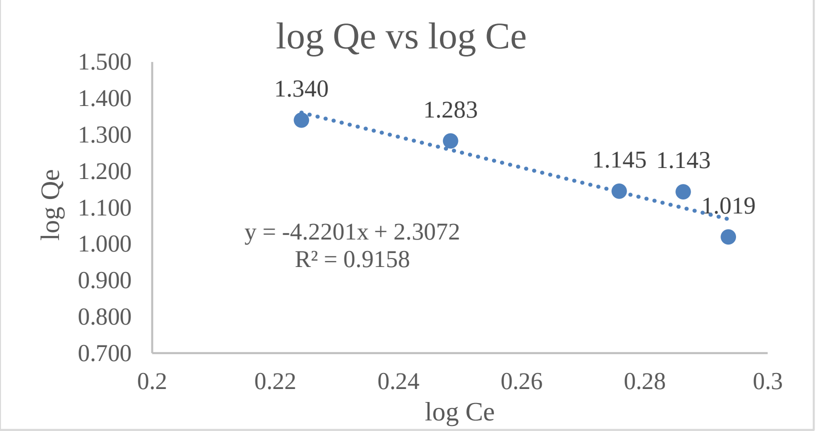


Figure 4.7 Graph of log Qe vs log Ce for Freundlich Isotherm

4.3 Biosorption Kinetic

Figure 4.8 shows the linear graph of log(q_e-q_t) against time which represents the pseudo first-order kinetic. It can be observed from the graph that the line deviates greatly from the linear trendline. Figure 4.9 showed the linear graph of t/q_t against time which represents the pseudo second-order kinetic. It can be observed from the graph that the line deviated less from the linear trendline.

By comparing the correlation coefficient, R^2 of both graphs which were 0.7035 and 0.9906, respectively, it was obvious that the pseudo second-order kinetic has better suitability to the description of the mechanism of the biosorption. Hence, the biosorption of nickel by *Cocos Nucifera L.* shoot can be illustrated by pseudo second-order kinetics which implied that the adsorption took place in second order mechanism and it was likely to be manipulated by chemical process.

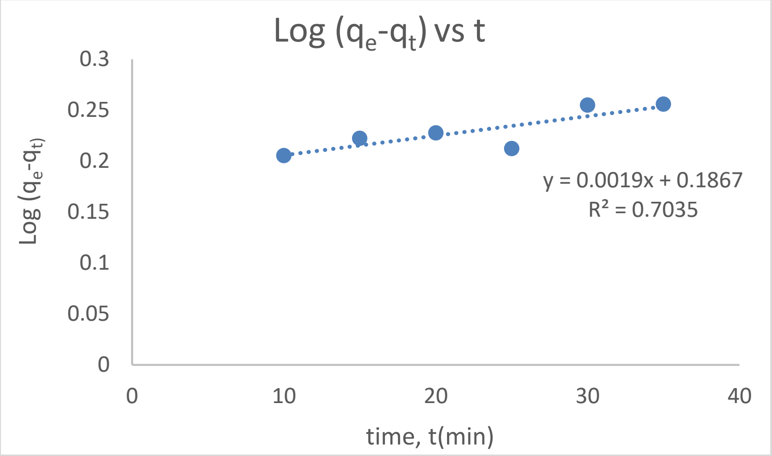


Figure 4.8 Pseudo First-Order Kinetics graph

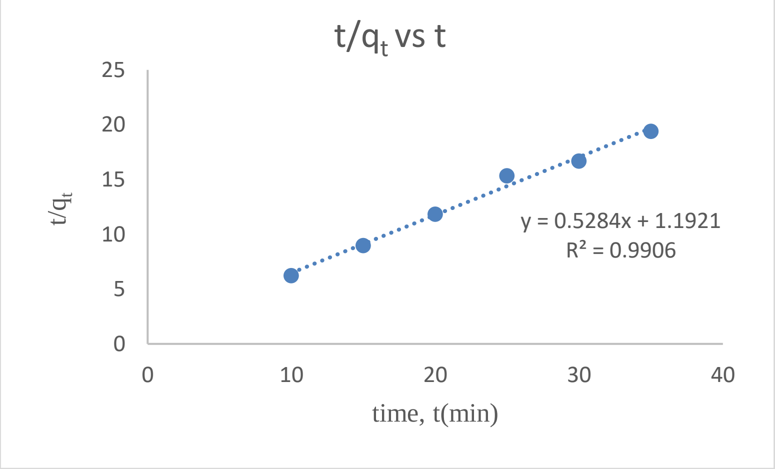


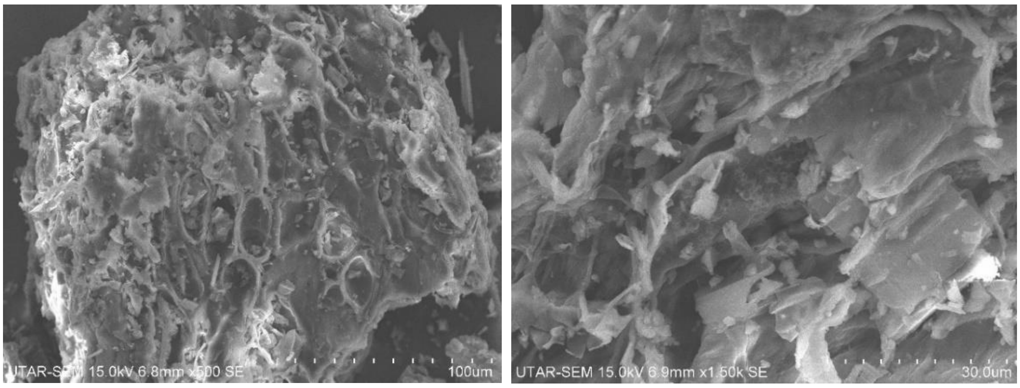
Figure 4.9 Pseudo Second-Order Kinetic Graph

4.4 Characterisation

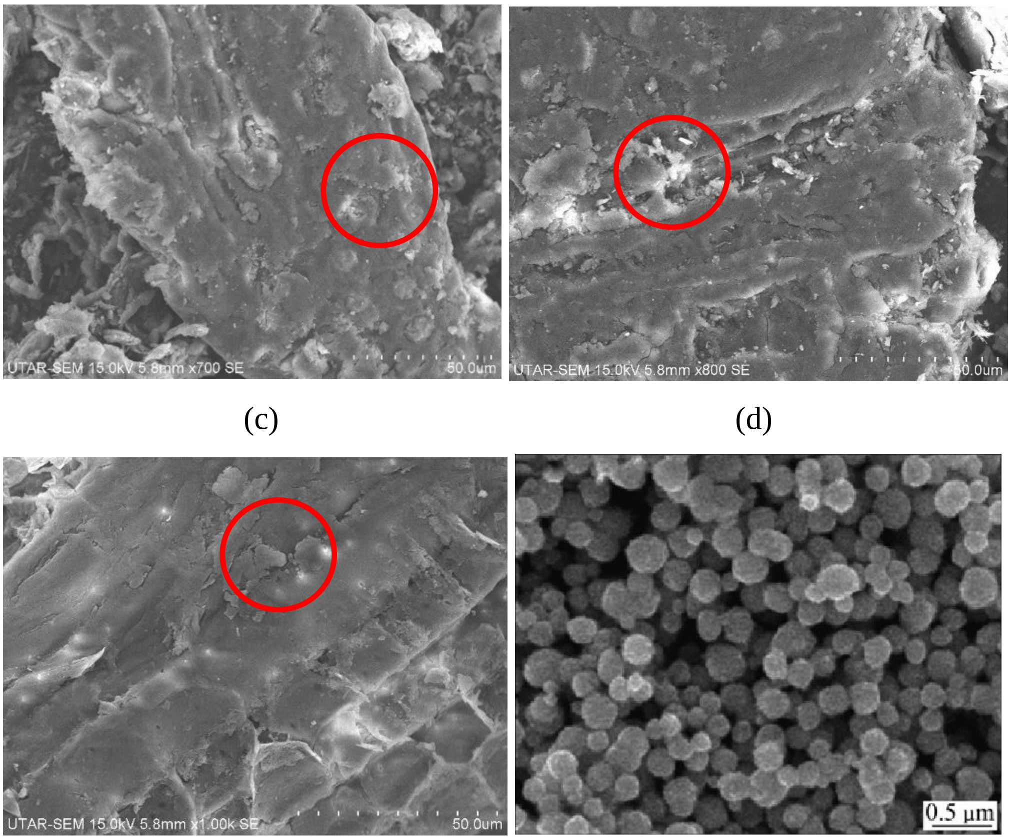
4.4.1 SEM

Figure 4.10(a) and (b) showed the morphology of *Cocos Nucifera L.* shoot before biosorption whereas Figure 4.10 (c) and (d) showed the morphology after biosorption. In Figure 4.10 (a) and (b), it can be observed that the surface morphology of *Cocos Nucifera L.* shoot was hollow with many pores on its rough surface. As the diameter of the pores exceeds 50 nm, it was an indication that the *Cocos Nucifera L.* shoot possessed macropore structure (Netzahuatl-Muñoz, Cristiani-Urbina and Cristiani-Urbina, 2015). The high number of irregularly shaped pores was ideal for adsorption due to the high surface area it offered.

As shown in Figure 4.10 (c), (d) and (e), *Cocos Nucifera L.* shoot after biosorption were seen to be swollen. Meanwhile, Figure 4.10 (f) showed the SEM micrograph of the nickel particles obtained from Huang et al., (2009). It was observed to be bright and have a very tiny round shape. Many bright spots can be observed on the *Cocos Nucifera L.* shoot after biosorption as marked in red in Figure 4.10 (c), (d) and (e), indicating that there were nickel particles in or on the *Cocos Nucifera L.* shoot. It showed that nickel particles were being adsorbed onto the surface of *Cocos Nucifera L.* shoot, be it the outer surface or the pore surface. This suggested that the main goal of this study was being achieved and nickel can be removed from aqueous solution by biosorption with *Cocos Nucifera L.* shoot.



(a) (b)



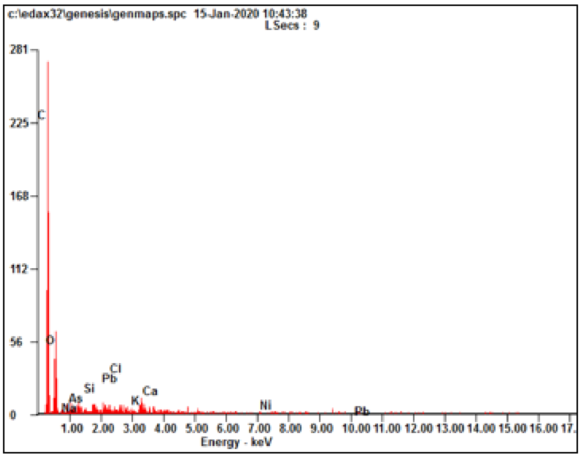
(c) (d)

(e) (f)

Figure 4.10 SEM morphology of (a-b) *Cocos Nucifera L.* shoot before biosorption ,(c-e) *Cocos Nucifera L.* shoot after biosorption and (f) nickel particle (Huang, et al., 2009)

4.4.2 EDX

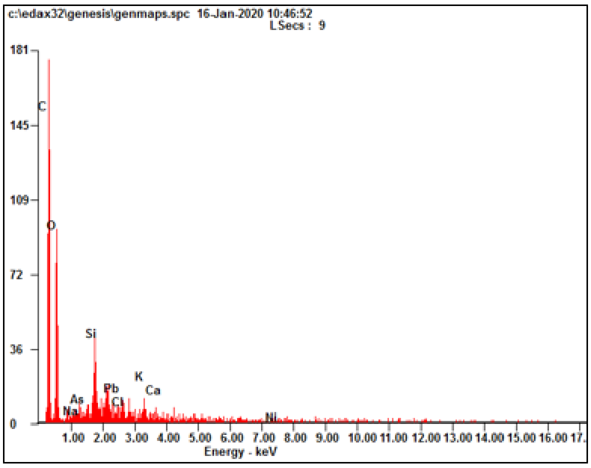
Figure 4.11 (a) and (b) showed the EDX result of *Cocos Nucifera L.* shoot before biosorption whereas Figure 4.11 (c) and (d) showed the EDX result of *Cocos Nucifera L.* shoot after biosorption. From Figure 4.11, it can be implied that the main compositions of *Cocos Nucifera L.* shoot are carbon and oxygen. It can be observed that that the nickel weight percentage in *Cocos Nucifera L.* shoot before biosorption is 0 %, showing that the absence of nickel. However, the nickel weight percentage in *Cocos Nucifera L.* shoot after biosorption is 0.85% which showed the presence of nickel. This indicated that nickel was adsorbed by *Cocos Nucifera L.* shoot.



(a)

Element	***Wt%***	***At%***
CK	63.75	73.36
OK	27.75	23.97
NaK	00.83	00.50
AsL	01.55	00.29
SiK	01.06	00.52
PbM	01.59	00.11
ClK	01.04	00.41
KK	01.47	00.52
CaK	00.95	00.33
NiK	00.00	00.00

(b)



(c)

Element	***Wt%***	***At%***
CK	53.67	63.30
OK	37.12	32.86
NaK	00.17	00.11
AsL	00.44	00.08
SiK	04.25	02.15
PbM	00.00	00.00
ClK	00.91	00.36
KK	01.71	00.62
CaK	00.87	00.31
NiK	00.85	00.21

(d)

Figure 4.11 EDX Element and Composition of Cocos Nucifera L. Shoot (a-b) Before And (c-d) After Biosorption

4.4.3 XRD

Figure 4.12 and 4.13 showed the XRD peak graph of *Cocos Nucifera L.* before and after biosorption, respectively. The broad peak between 10- 40° on both Figures 4.12 and 4.13 implied that the *Cocos Nucifera L.* shoot was in amorphous structure due to the presence of lignin in the sample. By comparing Figures 4.12 and 4.13 it can be observed that new peaks were formed at 26°, 34° and 45-55° which represented the presence of nickel particles (Rajagopal, et al., 2018). It was also observed that the intensities of peaks at 44-45° and 64-65° dropped significantly in Figure 4.13 as compare to in Figure 4.12. This might be due to the decrease in amount of vacant carbon and the replacement of calcium with nickel after biosorption.

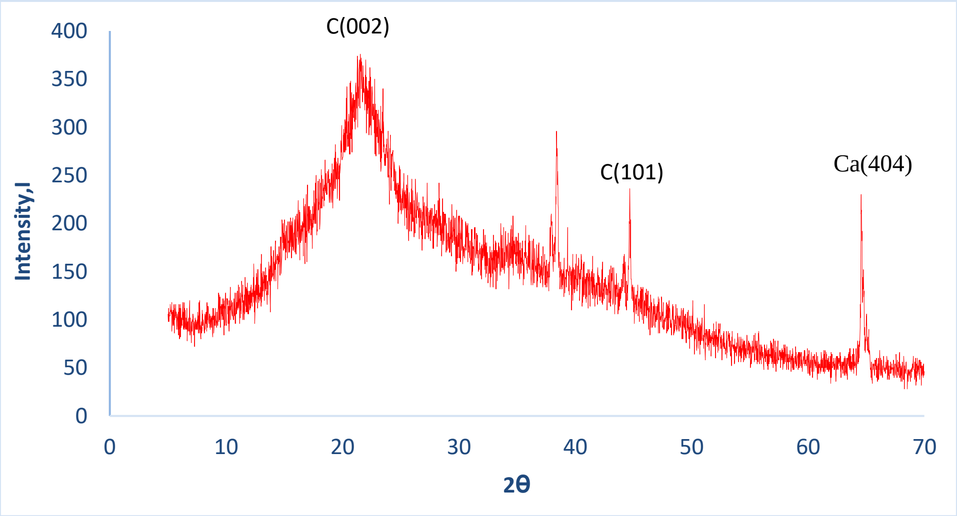


Figure 4.12 XRD graph of *Cocos Nucifera L.* shoot before biosorption

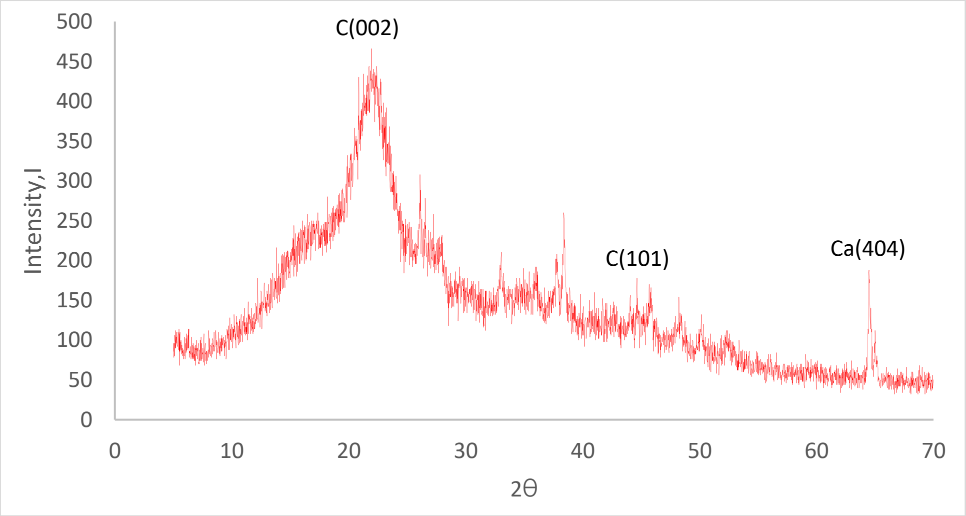


Figure 4.13 XRD graph of *Cocos Nucifera L.* shoot after biosorption

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

As a conclusion, the *Cocos Nucifera L.* shoot exhibited a great potential as a low-cost biosorbent in the removal of nickel from aqueous solutions. The batch experiment executed in this study has shown that the optimum pH for the removal of nickel by *Cocos Nucifera L.* shoot was at pH 9 with 89.56 % removal of nickel. The optimum biosorbent dosage and size to be added in 100 mL of 100 mg/L nickel solution was 25 g and 300 to 850 µm of size, with percentage of nickel removed at 89.56% and 90.87%, respectively. Besides, it was found that 30 minutes was the optimum contact time which gave 87.91 % removal of nickel. Meanwhile, it was concluded that the initial concentration of nickel did not significantly affect the biosorption efficiency of nickel by *Cocos Nucifera L.* shoot.

The morphology of *Cocos Nucifera L.* shoot was characterised by using SEM and XRD. It was found that *Cocos Nucifera L.* shoot possessed a hollow amorphous structure with rough microporous surface. It had many irregularly sized pores which was ideal for the adsorption process. On the other hand, the composition within the *Cocos Nucifera L.* shoot was analysed with EDX in which the *Cocos Nucifera L.* shoot mainly composed of carbon and oxygen, and there were nickel present after biosorption took place.

The biosorption of nickel by *Cocos Nucifera L.* shoot was concluded to be a monolayer adsorption in which the maximum adsorption takes place when the active sites are occupied. The kinetic data shown that the pseudo second-order kinetic model described the biosorption mechanism better with its correlation coefficient, R^2 value greater than 0.99. This can be deduced that chemisorption dominates the biosorption process.

5.2 Recommendations for future work

Throughout this study, the potential of *Cocos Nucifera L.* shoot as a low-cost biosorbent in the removal of nickel from aqueous solutions has been proven to be quite reliable. However, the characteristics of the *Cocos Nucifera L.* shoot and its biosorption efficiency can be further studied for improvement. Hence, there are several recommendations to be made to improve future work to provide a better understanding and insight of *Cocos Nucifera L.* shoot as a new low-cost biosorbent:

- More parameters such as temperature, agitation speed and etcetera can be studied in the interest of further understanding the impact of such parameters on the adsorption performance.
- Instead of just using nickel stock solution, experiments can be conducted by using real industrial wastewaters and polluted water to study its efficiency if it is to be implemented in the industry. The nickel removal efficiency can be studies along with the presence of other substances.
- Study of effect of physical or chemical pre-treatment of *Cocos Nucifera L.* shoot can be carried out to determine if pre-treatment can further enhance its biosorption capability.
- Characterisation of *Cocos Nucifera L.* shoot can be further extended to further understand the properties and characteristics of *Cocos Nucifera L.* shoot as well as to understand the biosorption mechanism that takes place.
- Application of *Cocos Nucifera L.* shoot as biosorbent in other type of heavy metal or organic compounds can be further explored.

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APPENDICES

APPENDIX A: Tables

Table A- 1 Experimental Data of pH Effect on Removal Efficiency

pH	**Initial Concentration, C_o (mg/L)**	**Equilibrium Concentration, C_e (mg/L)**	**Percentage Removal (%)**	**Metal Uptake Capacity, q_e (mg/L)**
2	100	40.28	59.72	1.4006336
4	100	21.22	78.78	1.6910368
6	100	21.53	78.47	1.6688686
7	100	25.93	74.07	1.5788968
9	100	17.45	82.55	1.730572
11	100	42.34	57.66	1.2937688

Table A- 2 Experimental Data of Biosorbent Dosage Effect on Removal Efficiency

Biosorbent Dosage (g)	**Initial Concentration, C_o (mg/L)**	**Equilibrium Concentration, C_e (mg/L)**	**Percentage Removal (%)**	**Metal Uptake Capacity, q_e (mg/L)**
5	100	21.87	78.13	1.676
10	100	19.19	80.81	1.772
15	100	13.95	86.05	1.888
20	100	13.91	86.09	1.933
25	100	10.44	89.56	1.966
30	100	9.666	90.334	1.981

Table A- 3 Experimental Data of Contact Time Effect on Removal Efficiency

Contact Time (min)	Initial Concentration, C_o (mg/L)	Equilibrium Concentration, C_e (mg/L)	Percentage Removal (%)	Metal Uptake Capacity, q_e (mg/L)
10	100	23.69	76.31	1.6048508
15	100	19.89	80.11	1.6682348
20	100	18.41	81.59	1.6896074
25	100	29.65	70.35	1.63
30	100	12.09	87.91	1.7983388
35	100	11.81	88.19	1.8030092

Table A- 4 Experimental Data of Initial Metal Concentration Effect on Removal Efficiency

Initial Concentration, C_o (mg/L)	Equilibrium Concentration, C_e (mg/L)	Percentage Removal (%)	Metal Uptake Capacity, q_e (mg/L)
20	6.034	93.966	0.29935288
40	10.04	89.96	0.6325328
60	14.08	85.92	0.9651456
80	18.81	81.19	1.2862492
100	18.41	81.59	1.6929212

Table A- 5 Experimental Data of Biosorbent Size Effect on Removal Efficiency

Biosorbent Size (µm)	Initial Concentration, C_o (mg/L)	Equilibrium Concentration, C_e (mg/L)	Percentage Removal (%)	Metal Uptake Capacity, q_e (mg/L)
300-850	100	9.128	90.872	1.84774496
850-1000	100	13.26	86.74	1.7788232
1 000-2000	100	11.38	88.62	1.8101816

Table A- 6 Langmuir Isotherm Result Data

Initial Concentration, C_o (mg/L)	**Equilibrium Concentration, C_e (mg/L)**	**Metal Uptake Capacity, q_e (mg/L)**	**Ce/q_e**
100	23.69	1.6048508	14.76
100	19.89	1.6682348	11.92
100	18.41	1.6896074	10.90
100	29.65	1.63	18.19
100	12.09	1.7983388	6.72
100	11.81	1.8030092	6.55

Table A- 7 Freundlich Isotherm Result Data

Initial Concentration, C_o (mg/L)	**Equilibrium Concentration, C_e (mg/L)**	**Metal Uptake Capacity, q_e (mg/L)**	**Log q_e**	**Log C_e**
100	23.69	1.6048508	0.205435	1.374565
100	19.89	1.6682348	0.222257	1.298635
100	18.41	1.6896074	0.227786	1.265054
100	29.65	1.63	0.212188	1.472025
100	12.09	1.7983388	0.254872	1.082426
100	11.81	1.8030092	0.255998	1.07225

Table A- 8 Pseudo Kinetic Model Data

Time (min)	**$q_e - q_t$**	**Log ($q_e - q_t$)**	**t/ q_t**
10	1.604851	0.205434663	6.231109
15	1.668235	0.222257176	8.99154
20	1.689607	0.227785803	11.83707
25	1.63	0.212187604	15.33742
30	1.798339	0.254871514	16.68206
35	1.803009	0.255997943	19.41199