

**A STUDY ON REMOVAL OF CU (II) AND NI (II) FROM SYNTHETIC  
WASTEWATER USING AGRO-WASTE AS LOW-COST POTENTIAL  
ADSORBENT**

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

**Lee Kong Chian Faculty of Engineering and Science  
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**May 2019**

**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**

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## ABSTRACT

Electroplating industry has been generating increasing amount of wastewater containing toxic heavy metals like copper and nickel ions which had led to water quality deterioration. There is a growing demand of recycling agro-wastes as potential adsorbents due to their high availability at no cost and efficiency in heavy metal removal. In this project, the removal of copper and nickel ions from synthetic wastewater was explored with spent coffee ground (SCG), eggshell waste and papaya seeds as adsorbents. Their morphologies and functional groups were characterised using scanning electron microscopy (SEM) and fourier transform infrared spectroscopy (FTIR), respectively. It was found that adsorption performance varied at different pH. It was also discovered that increasing initial metal concentration and adsorbent dosage presented negative effect on adsorption performances. The optimum contact time of adsorption was found to be 30 min. The selectivity study showed that SCG and papaya seeds had higher affinity towards Cu (II), whereas eggshell waste had higher affinity towards Ni (II). Besides, the experimental data was fitted into Langmuir and Freundlich isotherm models. It was discovered that the data was best fitted into Langmuir isotherm model and the maximum adsorption capacities of the agro-wastes adsorbents could be determined. In addition, the kinetics data was fitted into pseudo-first-order and pseudo-second-order kinetics models. The data proved that the adsorption process was well-described by the pseudo-second-order model.

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**LIST OF SYMBOLS / ABBREVIATIONS**

$Q_e$	amount of adsorbent adsorbed at equilibrium, mg/g
$Q_t$	amount of metal ions adsorbed at any time $t$ , mg/g
$Q_{max}$	maximum adsorption capacity, mg/g
$C_e$	concentration of solute after reaching equilibrium, mg/L
$C_o$	initial concentration of metal ion in liquid sample, mg/L
$K_L$	adsorption energy, L/mg
$k$	Freundlich constant representing adsorption capacity
$n$	Freundlich constant representing adsorption intensity
$k_1$	rate constant of pseudo-first-order equation, $\text{min}^{-1}$
$k_2$	rate constant of pseudo-second-order equation, $\text{min}^{-1}$
AC	activated carbon
CAGR	compound annual growth rate
Cu (II)	copper ion
Ni (II)	nickel ion
SCG	spent coffee ground

## CHAPTER 1

### INTRODUCTION

#### 1.1 General Introduction

In recent decades, water quality deterioration has become a great concern in sustainable development. From previous study, it is found that industrial waste constitutes the primary sources of heavy metal water pollution (Bhuyan and Islam, 2017). Owing to rapid industrialization, unplanned urbanization, population growth and anthropogenic activities, the utilization of heavy metals in industries such as mining operation, electroplating, and metal processing has tremendously increased (Kyzas et al., 2013; Carolina et al., 2017). These industries also utilize ample amount of water in their production, and thus large amount of wastewater will also be generated and discharged to the environment. As a consequence, this will lead to heavy metal water pollution.

Heavy metals are chemical elements having specific gravity which are at least 5 times the water specific gravity. They are very toxic and poisonous to human health as well as the aquatic organisms even at trace concentrations (Ushakumary, 2013). Heavy metal ions can easily seep into the surface water, groundwater and soil–plant ecological systems, which will cause accumulation of metal ions in aquatic organisms, animals, plants, and human beings (Mohanraj, Azeez and Priscilla, 2004; Zereini et al., 2005; Jeon, 2017). This poses serious threat to the global ecosystems and may lead to severe ecological imbalance (Kyzas et al., 2013). Therefore, it is a must to eliminate the heavy metal ions before discharging the wastewater. Some examples of heavy metal ions are copper, lead, zinc, nickel, cadmium, chromium and many more.

Owing to the persistence, toxicity and non-biodegradable nature of heavy metal ions, heavy metal removal from polluted water has become a hot topic for researchers in the past few decades (Patterer et al., 2017). There is a myriad of conventional methods employed in heavy metal removal including chemical oxidation and reduction, membrane separation, adsorption, ion exchange, electrolytic treatment and electro-precipitation (Babel and Kurniawan, 2003). Among these techniques, adsorption has been reported to be more economical and efficient for heavy metal removal in wastewater treatment.

Conventional adsorbents such as activated carbon, chitosan, zeolite and silico-aluminous materials are frequently used for adsorption process. Of all the adsorbents, activated carbon is the most commonly used. Activated carbon is very ideal adsorbent for its high adsorption capacity, abrasion resistance, thermal stability and porosity. However, it also has drawbacks such as expensive cost and loss of adsorbent during regeneration.

Over the past few years, the research community has shifted their research interest towards alternative agro-waste such as agricultural residues, plant materials, and waste biomass sources for heavy metal removal in wastewater treatment. The primary reason is abundant amount of these agro-wastes can be easily collected without any cost due to their high annual production and consumption. Various types of agro-wastes had been explored for their reusability in heavy metal elimination. For instances, orange peel, tea waste, peanut hull and so forth.

## **1.2 Importance of the Study**

It is very significant to conduct this study as heavy metals in wastewater are very poisonous to human health and the environment. Moreover, the world is now scarce of clean water. Thus, from the viewpoint of environmental protection and resource conservation, effective recycling and reusing the wastewater have become an urge.

Agro-waste has been one of the most popular low-cost adsorbents to treat wastewater. Hence, this study is also important to determine the feasibility of agro-waste as low-cost adsorbent for heavy metal removal. If this method is feasible, it will be a greener and more economical way as it does not require extra chemical use and helps to save wastewater treatment costs.

## **1.3 Problem Statement**

The electroplating industry has generated ample amount of wastewater, which caused serious heavy metal water pollution. Therefore, wastewater needs to be treated before discharging. Adsorption process is found to be the most efficient way.

However, the cost of conventional adsorbents such as activated carbon and zeolite are so expensive that researchers start to look for low-cost adsorbent to replace them. Agro-waste is most likely to be utilized as it is highly available at no cost, and efficient in heavy metal removal. The reuse of agro-waste as adsorbent can

also help to reduce the amount of waste as it may cause secondary pollution to the environment if accumulation happens.

#### **1.4 Aim and Objectives**

The aim of this project was to investigate the potential use of SCG, papaya seeds and eggshell waste as adsorbent to remove copper and nickel ions from synthetic wastewater.

The objectives of this project were listed below:

1. To characterise the morphology and functional groups of SCG, eggshell waste and papaya seeds using scanning electron microscopy (SEM) and Fourier transform infrared (FTIR), respectively.
2. To investigate the effects of pH, initial concentration, adsorbent dosage and contact time on the adsorption performance of SCG, eggshell waste and papaya seeds.
3. To compare the selectivity of SCG, eggshell waste and papaya seeds towards the adsorption of copper and nickel ions from binary-metal synthetic wastewater.
4. To determine the best fitting isotherm model using the adsorption data for SCG, eggshell waste and papaya seeds as adsorbent.
5. To identify the best fitting kinetics model using the adsorption data for SCG, eggshell waste and papaya seeds as adsorbent.

#### **1.5 Scope and Limitation of the Study**

The scopes of this study included the methodology of the experiment, characterisation of adsorbent and data analysis. Copper and nickel metal ions were selected for the study for they were typically found in electroplating wastewater. SCG, eggshell waste and papaya seeds were selected as the adsorbents in this research due to their high obtainability. Several factors affecting the adsorption performance such as pH, initial metal concentration, adsorbent dosage, contact time and selectivity of metal adsorption were investigated. The adsorption experiments were conducted in batch mode.

The limitation of study would be the time constraint. Continuous adsorption experiment was not performed as it could be very time-consuming. In addition, the parameter study of different particle size on adsorption performance was not

performed due to lack of different sizes of sieves. The porosity of adsorbent was also not studied as the Brunauer, Emmett and Teller (BET) analyser was not functioning.

## **1.6 Contribution of the Study**

Through this research, the water deterioration issue due to presence of abundant heavy metal ions, was expected to be curbed by exploring the reusability of agro-wastes as low-cost adsorbents. Not only will this study help to reduce the dependence on high cost adsorbents in heavy metal removal, the possible environmental problems caused by the agro-wastes may be minimised as well.

## **1.7 Outline of the Report**

The outline of report was categorised into four major sections as follow:

- Chapter 2 covered on the up-to-date literature review on areas related to the study, such as the background of electroplating wastewater, conventional heavy metal removal techniques, different types of adsorption and adsorbents, as well as the adsorption isotherm and kinetic models.
- Chapter 3 showed the methodologies and work plan of this project, which includes the preparation of synthetic wastewater and adsorbents, characterisation techniques, parameters to be investigated in the adsorption experiment and the equations of adsorption isotherm and kinetic models.
- Chapter 4 discussed the results from each parameter study, selectivity study and adsorption process using adsorption isotherm and kinetic models.
- Chapter 5 concluded the major findings from each parameter study, selectivity study, adsorption process and propose the optimum experimental conditions for heavy metal ions removal. Recommendations and suggestions were also given to improve the project in future

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Background of Electroplating Wastewater

Wastewater containing heavy metals comes from different industries namely, textile dyeing, mining operation, production of paints and pigments, production of storage batteries, ceramic and glass industries, metal-processing industries and electroplating (Cerino-Córdova et al., 2013; Kyzas et al., 2013). Today, there are many industries which adopt the modern electroplating technology. For instance, the aerospace applications, manufacturing of instruments, mechanical engineering and power generation (May, 2018). Needless to say, the electronics industry still highly relies on electroplating for the fabrication of printed circuit boards and semiconductors (California State University, 1986).

Electroplating is a process which deposits a thin metal coating on the surface of another metal by using electrical current through an electrolytic bath. It involves an anode and a cathode, in which their terminals are immersed in electrolytic bath that contains metal ions to be coated (Safe Work Australia, 2012). The major purpose of electroplating is to enhance the appearance of metal surface, improve the resistance to abrasion and corrosion or the combination of them (Sivasangari et al., 2016). In electroplating process, dissolution of metal from anode deposits the metal ions on the cathode. After electroplating process, the wastewater is usually disposed to the environment without any treatment, and thus it leads to water pollution.



Figure 2.1: Simplified Diagram of Industrial Electroplating Process (American Plating Company, n.d.)

There are two main types of electroplating wastewater, namely bath solutions and rinse water. The discharge of rinse water is continuous and it contains low concentration of heavy metals. On contrary, bath solutions contain significantly higher concentration of heavy metals (up to hundreds of g/L). The constituents of wastewater vary depending on the metals and chemical baths used for electroplating. Table 2.1 presents the typical composition of electroplating wastewater. The

composition of copper and nickel are higher than other heavy metal ions, especially copper.

Table 2.1: Typical Composition of Electroplating Wastewater

<b>Heavy metal ion</b>	<b>Composition (mg/L)</b>
Chromium	0.19
Nickel	5.82
Copper	12.94
Cadmium	0.03

Source: Husain, Javed and Khan (2014)

The heavy metal ions in electroplating wastewater are very hazardous and toxic to human health, other living organisms and the environment. Malaysian Environmental Quality (Industrial Effluent) Regulations, 2009 was established to regulate the discharge of industrial effluents and minimise the impact of the hazardous chemicals towards human and the environment. Table 2.2 shows the maximum discharge limit of industrial effluent under the regulation aforementioned.

Table 2.2: Permissible Limit for Industrial or Mixed Effluent Discharge for Standards A and B

<b>Heavy metals</b>	<b>Permissible limit for industrial or mixed effluent discharge (mg/L)</b>	
	<b>A</b>	<b>B</b>
Mercury	0.005	0.05
Cadmium	0.01	0.02
Chromium, Hexavalent	0.05	0.05
Chromium, Trivalent	0.20	1.0
Arsenic	0.05	0.10
Cyanide	0.05	0.10
Lead	0.10	0.5
Copper	0.20	1.0
Manganese	0.20	1.0
Nickel	0.20	1.0
Tin	0.20	1.0
Zinc	2.0	2.0
Boron	1.0	4.0
Iron	1.0	5.0
Silver	0.1	1.0
Aluminium	10	15
Selenium	0.02	0.5
Barium	1.0	2.0

Source: Department of Environment (DOE) Malaysia (2009)

Based on the Environmental Quality (Industrial Effluent) Regulations, 2009, the concentration of industrial effluent must not exceed the safe permissible limit listed in Table 2.1. Standard A is applicable to industrial effluent which is discharged into any inland waters within the catchment areas specified by the Environmental Quality Council. Meanwhile, Standard B is applicable to industrial effluent which is discharged into whichever inland or Malaysian waters.

For heavy metals in industrial effluents like copper, nickel and zinc, there is an additional regulation pursuant to the subregulation mentioned above. The total concentration of mixed effluent which consists of two or more metals must not exceed 0.5 and 3.0 mg/L for Standards A and B, respectively (Department of Environment Malaysia, 2009).

Heavy metals like copper and nickel are especially found in abundance in electroplating wastewater as these metals are commonly used for electroplating process. As such, the health effects and environmental impacts of these metals should be further explored.

### **2.1.1 Copper**

Copper is a reddish transition metal in Period 4 Group 11 with the atomic number of 29, atomic weight of 63.5 and density of 8.96 g/cm<sup>3</sup>. Its boiling point is at 2595 °C and melting point at 1083 °C (Royal Society of Chemistry, n.d.). Copper metal is ductile, malleable and has excellent thermal and electrical conductivity. It has many commercial applications, such as making electrical wiring, pipes, cooking utensils, building materials and so forth (World Health Organization, 2004).

Copper is also an important trace element to support animal and plant growth. Small amount of copper compounds is added to fertilizers and animal feed as nutrients for animal and plant growth (Landner and Lindstrom, 1999; ATSDR, 2002). However, excess concentration of copper release to environment becomes very toxic to the flora and fauna. High intake of copper by human may lead to diseases like insomnia, liver damage, Wilson disease and so forth.

Wastewater sources containing copper ions are mostly produced from copper polishing, electroplating, paint manufacturing, printed circuit board manufacturing, printing operations, wire drawing, wood preservative using and printing operations. The typical concentration of copper discharged may range from less than 1 ppm of copper cleaning operation up to several thousand mg/L of electroplating bath waste (Salmani et al., 2012).

### **2.1.1.1 Health Effects**

Copper is a vital trace element for proper functioning of organs and human metabolism. However, excess copper intake becomes very crucial to human health. He or she who ingested very high concentration of copper salts may develop symptoms such as headache, dizziness, nausea, abdominal pain, respiratory difficulty, vomiting and diarrhoea. In even worse case, it will cause diseases, such as tachycardia, haemolytic anaemia, massive gastrointestinal bleeding, failure of liver and kidney system, and eventually lead to death. There was a case of a young male adult diagnosed with liver failure due to chronic copper poisoning. He was said to be taking 30-60 mg/L of copper daily as mineral supplement for 3 years (World Health Organization, 2014).

### **2.1.1.2 Environmental Impacts**

Abundant amount of copper metal in water will affect the marine and freshwater organisms like fish and molluscs. Sub-lethal copper concentration will impose chronic impact on the aquatic animals by causing impairment to their gills, kidneys, liver and even nervous system. Moreover, high copper level will also cause interference to the sense of smell in fish, which prevents them from finding their routes to the mating areas or choosing good mates (Solomon, 2009). Each fish species will have different sensitivity level towards copper. For instance, LD50 of tilapia for a 96-hour exposure to copper sulphate is approximately 58 mg/L, while for catfish, LD50 is around 70 mg/L.

## **2.1.2 Nickel**

Nickel is a silver-white transition metal in Period 4 Group 10 with the atomic number of 28, atomic weight of 58.693 and density of 8.90 g/cm<sup>3</sup>. Its boiling point is at 2913 °C and melting point at 1455 °C (Royal Society of Chemistry, n.d.). It is a naturally occurring element which can exist in different mineral forms (Cempel and Nikel, 2006). Its prevalent oxidation state under environmental condition is +2 valence state, even though it can exist in different oxidation states (-1, +1, +3 and +4).

There are many applications and commercial uses of nickel metal. It can be used to produce intermediate or final product. More than 80% the intermediate nickel use goes into steels and alloys production (United States Environmental Protection

Agency, 1984. Nickel is known as its high resistance to corrosion, strength, and high ductility, which make it a highly valuable alloying element. Meanwhile, for the end use of nickel, more than 90% of it is used as metal alloys for the production of equipment parts exposed to corrosive chemicals (United States Environmental Protection Agency, 1984). For instance, petroleum refining and manufacture of chemicals and allied products. Anthropogenic nickel sources come from nickel ore mining and smelting, nickel matte refining, recover of secondary or co-product nickel, nonferrous metals production, battery manufacturing, nickel chemical manufacturing and electroplating (United States Environmental Protection Agency, 1984).

### **2.1.2.1 Health Effects**

Nickel may cause adverse impacts on human health, particularly allergic reaction. Skin contact with nickel contaminated water will result in skin rash, hand eczema and allergic dermatitis. People who are allergic with nickel may have reactions when having prolonged skin contact with nickel or even food intake containing nickel. Meanwhile, for those who are not sensitive to nickel, very large amount of nickel intake will cause them harmful health effects (ATSDR, 2005). Excess nickel uptake will lead to various pathologic effects such as cardiovascular and kidney diseases, cancer, lung fibrosis and many more.



Figure 2.2: Skin Rashes Caused by Nickel Allergy (OMICS International, n.d.)

### **2.1.2.2 Environmental Impacts**

Nickel is easily accumulated in the biota, especially in phytoplankton and other aquatic plants, which indicate the occurrence of water contamination. When nickel is discharged into the environment by the industries, it is most likely to be distributed evenly through the soil profile (Cempel and Nikel, 2006). As nickel is quite mobile in acidic organic rich soils, it will affect the quality of groundwater.

When nickel was released to the river, it was transported as precipitated coating on the particles. It was found that the nickel concentrations in the largest and only navigable river in the South of Iran (River Karoon) increase from 69.3 to 110.7  $\mu\text{g/L}$  during winter, and from 41.0 to 60.7  $\mu\text{g/L}$  during spring. It was clear that the water pollution was worsening as nickel was transported along the river, down to the estuary at Persian Gulf (Diagomanolin, 2004). In addition, the average Ni concentration increased from 0.7 to 1.08  $\mu\text{g/L}$  when nickel in the rivers flows into the Baltic Sea in Poland (Szefer, 2002; Gaillardet et al., 2003). The nickel content in sea water was usually at concentrations of 0.1- 0.5  $\mu\text{g/L}$  (Cempel and Nikel, 2006).

## **2.2 Conventional Heavy Metal Removal Techniques**

There are several conventional methods for heavy metal ions removal from electroplating wastewater. For example, electrocoagulation (EC), ion exchange, membrane technologies (reverse osmosis and ultrafiltration), precipitation and clarification techniques, adsorption and so forth. Table 2.3 lists the advantages and disadvantages of different conventional heavy metal removal techniques.

Table 2.3: Advantages and Disadvantages of Conventional Heavy Removal Techniques

Techniques	Advantages	Disadvantages	Reference
Electrocoagulation (EC)	<ul style="list-style-type: none"> <li>• Effective in removing small colloidal particles</li> <li>• Chemical use is not needed</li> <li>• Produce less sludge</li> </ul>	<ul style="list-style-type: none"> <li>• Frequent replacement of electrode</li> <li>• Loss of efficiency due to formation of impermeable oxide film on cathode</li> <li>• High utility cost</li> </ul>	Siringi et al. (2012); Wang et al. (2004)
Ion exchange process	<ul style="list-style-type: none"> <li>• Widely applied for heavy metal removal</li> <li>• Ion-exchange resins can be regenerated</li> </ul>	<ul style="list-style-type: none"> <li>• Fouling of ion-exchange resins may happen due to presence of precipitates such as calcium sulphate and ferric oxide</li> <li>• Replacement of resin ions needed in every cycle.</li> <li>• Very expensive</li> </ul>	Ushakumary (2013); Nguyen et al. (2013)
Membrane process	<ul style="list-style-type: none"> <li>• High heavy metal ions removal efficiency</li> </ul>	<ul style="list-style-type: none"> <li>• Remove only low metal ions concentration</li> <li>• Membrane scaling happens when metal concentration increases</li> <li>• High energy and cost required to treat the membrane</li> </ul>	Ushakumary (2013)

Table 2.3: Continued.

Techniques	Advantages	Disadvantages	Reference
Precipitation and clarification techniques	<ul style="list-style-type: none"> <li>• Simplicity</li> <li>• Inexpensive capital cost</li> <li>• Adapted to treat high heavy metal ions concentration</li> </ul>	<ul style="list-style-type: none"> <li>• Cannot remove complex metals</li> <li>• Ineffective in removing very low metal concentration in wastewater</li> <li>• Large amount of chemicals required for precipitation</li> <li>• High cost of precipitation</li> </ul>	Kurniawan et al. (2006); Ushakumary (2013)
Adsorption	<ul style="list-style-type: none"> <li>• Wide pH range</li> <li>• High metal binding capacity</li> <li>• Low cost</li> <li>• Easy to operate</li> </ul>	<ul style="list-style-type: none"> <li>• Removal of heavy metals from low wastewater concentration</li> <li>• Adsorption efficiency depends on the type of adsorbents</li> <li>• Low selectivity</li> </ul>	Kurniawan and Babel (2003); Aklil, Mouflihb and Sebti (2004); Ushakumary (2013)

## **2.3 Adsorption**

Adsorption is one of the most promising heavy metal removal techniques because of its high efficiency and selectivity to remove certain type of metal, while requiring low capital and operation costs. This is so as the design of adsorption system is very simple and easy to operate (Ushakumary, 2013). Easy reuse or recovery of adsorbent after adsorption helps to minimise the operating cost. According to Ushakumary (2013), adsorption process can be operated under a wide pH range (pH 2-9) and temperatures (4 – 90 °C).

Adsorption is a process which takes place at an interface between any two phases such as liquid-liquid, gas-liquid or solid-liquid interfaces (Barakat, 2011). It is also defined as separation process in adsorbent suspended with solid particles, which the adsorbate is transferred from the bulk fluid phase to the surface of the adsorbent particles. The molecules of bulk fluid phase tend to attach and accumulate on the surface of the solid particles when the solid surfaces are exposed to fluid phases. There are two different kinds of adsorption, which are physical adsorption and chemical adsorption (Jiaping, 2012).

### **2.3.1 Physical Adsorption**

Physical adsorption is the adsorption of molecules on the adsorbent particles surfaces as a result of intermolecular forces of attraction (Ushakumary, 2013). It is also known as the Van der Waals adsorption. Physical adsorption is often an exothermic process. The energy involved between adsorbate and adsorbent is usually the same magnitude but is normally a bit higher than the energy condensation of the adsorbents. Thus, activation energy is not required because generally physical adsorption system can achieve thermodynamic equilibrium fairly and rapidly. The adsorption energy is usually within 80 kJ/mole, with typical energies being considerably less (Webb, 2003).

In physical adsorption, the molecules are not specifically adsorbed onto a binding site of the adsorbent surface. The molecules diffuse along the adsorbent surface. Physical adsorption is readily reversible because it is only weakly bound by Van der Waals forces (Webb, 2003). This reversibility nature has been applied to several industrial adsorption operations such as regeneration of adsorbed substances, recovery of adsorbents to reuse and fractionation of mixtures (Ushakumary, 2013). Undoubtedly, it helps to minimise the extraction of virgin materials and maximise

the potential of used materials. Molecules which are physically adsorbed will retain its identity and recover to its original form in the fluid phase when desorption is performed. Moreover, physical adsorption can occur on any interface as long as the temperature and pressure conditions are favourable. It occurs as a multilayer at relatively high pressure (Webb, 2003).

### **2.3.2 Chemical Adsorption**

Chemical adsorption, also known as chemisorption, involves chemical interaction between the adsorbate and adsorbent surface (Ushakumary, 2013). It has higher adsorption energy than purely physical adsorption. Heat of adsorption for C-N bond can reach up to 600 kJ/mole and 800 kJ/mole for chemical bonds (Webb, 2003). The chemical bonds are formed by electrons sharing between the adsorbate and adsorbent, and the bonds result in formation of surface compound.

In chemisorption, chemical reaction takes place so that the molecules are able to attach onto specific binding sites of the adsorbents. Unlike physical adsorption, chemisorption is irreversible due to its bond strength. Chemically adsorbed molecules will lose their identities and cannot return to original form by desorption. Furthermore, chemisorption is highly selective. It only occurs between specific pairs of adsorbate and adsorbent or when chemically active surface is free of previously adsorbed species (Webb, 2003). Chemisorption is a single-layer process, which only occurs when the adsorptive species makes direct contact with the surface except for highly polar adsorptive like  $\text{NH}_3$  (Webb, 2003).

In chemisorption, large activation energy is required due to insufficient thermal energy to achieve thermodynamic equilibrium at low temperature. Chemisorption may be exothermic or endothermic as a wide range of energy is involved. The energy of chemisorption is roughly equal to the energy involved in a comparable chemical reaction.

### **2.3.3 Factors Affecting Adsorption**

There are some factors that will have impact on the adsorption, such as surface area of adsorbent (particle size), pH, initial concentration, adsorbent dosage and contact time.

Surface area of the adsorbents is a key factor that affects the adsorption process. Smaller particles size of adsorbents will have larger surface area exposed,

thus, improves the adsorption performance. Hence, more heavy metal ions can be removed. Larger particle size will have lower adsorption performance as large metal ions are unable to enter every initial pore of the adsorbent (Ushakumary, 2013).

Furthermore, pH value also greatly affects the adsorption performance. The active sites of the adsorbent surface as well as the property of adsorbents will be affected by pH. The influence of pH is indicated by the charge on the adsorbent surface (Ushakumary, 2013). At low pH, negatively charged adsorbent surface will be neutralized by large number of H<sup>+</sup> ions. This enhances diffusion and adsorption process. On contrary, at high pH, competition happens between the H<sup>+</sup> ions and the positively charged adsorbent surface and leads to a decline in adsorption performance (Jiaping, 2012).

Moreover, initial metal ions concentration is also another factor which affects adsorption. The initial concentration of metal ions delivers a driving force that enables the transport of heavy metal ions from the adsorbate to the adsorbent surface (Sahmoune, Louhab and Boukhiar, 2011; Taha, Arifien and El-Nahas, 2011). When the initial metal ions concentration increases, the adsorption performance of the adsorbent increases.

Adsorbent dosage also has major effect on the adsorption process. When adsorbent dosage increases, the adsorption of metals also increases. There are several reports that proved this statement. For example, according to a study conducted by Kumar et al. (2012), it is discovered that the removal of Cd (II) increased quickly with the increase in cashew nut shell dosage. This is explained by the high number of adsorption sites due to high adsorbent dosage.

Another factor that affects adsorption is contact time. When the contact time between adsorbent and adsorbate increases, the adsorption of heavy metal ions also increases until it reaches equilibrium. Equilibrium time is achieved whenever the adsorption reaches a state of dynamic equilibrium with desorption. It is a very critical factor because it indicates the maximum adsorption capacity of adsorbent, which all the adsorption sites are occupied with the metal ions to be adsorbed (Azouaou et al., 2010; Maria Martinez et al., 2006; Mohammad Mehdi et al., 2011). Longer contact time does not entirely represents better adsorption. The optimum contact time for better adsorption actually corresponds to the types of adsorbents used.

Selectivity of adsorbents towards certain metal ions could have an impact on adsorption. Several studies had shown that different adsorbents might have different

affinity towards different metal ions. For instances, according to Mosa et al. (2011), cotton stalks had better selectivity towards Pb (II) adsorption than Mn (II). Moreover, Taha et al. (2011) discovered the selectivity could also be associated with the hydrated ionic radii of the metal ions to be adsorbed. He found that potato peels had better selectivity towards Pb (II), followed by Cd (II) and Zn (II). However, the hydrated radii decreased from Zn (II) to Pb (II). Hence, the selectivity of adsorbents towards metals increased with their decreasing hydrated radii.

## **2.4 Adsorbents**

There is a variety of adsorbents that are employed in the industry for heavy metal removal. These adsorbents can be categorised into activated carbon (AC), natural source adsorbents, agro-waste adsorbents, biomass adsorbents and by-product adsorbents.

Agro-waste is waste generated by agriculture activities such as farming activities and is often disposed to the landfill (Lim and Matu, 2015). Nowadays, a wide range of agro-wastes have been studied for their efficiency in eliminating different metal ions from wastewater with the goal to replace AC. Table 2.4 demonstrates the adsorption capacity of different agro-wastes for copper and nickel removal from wastewater.

Table 2.4: Adsorption Capacity of Various Agro-wastes for Copper and Nickel Removal

<b>Metal Ions</b>	<b>Agro-waste</b>	<b>Adsorption Capacity (mg/g)</b>	<b>Reference</b>
<b>Cu (II)</b>	Orange peel	50.94	Liang et al. (2009)
	Mango peel	46.09	Iqbal, Saeed and Kalim (2009)
	Tea waste	48.00	Amarasinghe and Williams (2007)
	Wheat bran	17.42	Aydn, Bulut and Yerlikaya (2008)
	Peanut hull	21.25	Zhu, Wang and Chen (2009)
	Chestnut shell	12.56	Yao, Qi and Wang (2010)
<b>Ni (II)</b>	Orange peel	158.00	Ajmal et al. (2000)
	Mango peel	39.75	Iqbal, Saeed and Kalim (2009)
	Pomegranate peel	52.00	Bhatnagar and Minocha (2010)
	Tea waste	73.00	Ahluwalia and Goyal (2005)
	Guava seed	18.05	Ramana et al. (2010)

In this project, spent coffee ground, papaya seeds and eggshell waste had been selected as the potential low-cost adsorbents for the removal of copper and nickel from synthetic electroplating wastewater.

#### **2.4.1 Spent Coffee Ground (SCG)**

Coffee is one of the most consumed and popular drinks worldwide. The growing number of large international coffee shops in the market such as Starbucks, Coffee Bean and Costa Coffee undeniably nurtures global coffee drinking culture. Table 2.5 shows the world coffee consumption around the world from 2013 to 2017, as well as the compound annual growth rate (CAGR).

Table 2.5: World Coffee Consumption and Compound Annual Growth Rate (CAGR)

<b>Year</b>	<b>2013/14</b>	<b>2014/15</b>	<b>2015/16</b>	<b>2016/17</b>	<b>CAGR (%)</b>
World Total Consumption (in thousands 60 kg bags)	148889	151828	155712	157858	2.0
Europe	50179	50914	51674	51860	1.1
Asia & Oceania	30697	32641	33628	34680	4.2
North America	27706	27363	28934	29564	2.2
South America	24682	24960	25248	25398	1.0
Africa	10497	10713	10926	11119	1.9
Central America & Mexico	5128	5237	5302	5239	0.7

Source: International Coffee Organization (2018)

From Table 2.5, it was clearly demonstrated that Europe consumed the most coffee over the years from 2013 to 2017. Asian countries were ranked second behind European countries with the CAGR of 4.2%. The overall trend of coffee consumption is expected to rise even more in next few years. In Malaysia, coffee drinking culture is growing year by year. The average coffee consumption for each Malaysian is 2.5 cups of coffee per day (The Sun, 2017). Owing to the high consumption of coffee, large amount of Spent Coffee Ground (SCG) is generated. This leads to world annual production of 6 million tons of SCGs (Mussatto et al., 2011).

SCG is the coffee residue obtained after treating the coffee powder with steam or hot water for instant coffee preparation (Mussatto et al., 2011). It constituted nearly 50% of the coffee cherry fruit waste. Another 50% is made of coffee husk, skin, pulp, silverskin, mucilage and hull. Figure 2.3 shows the cross-section of coffee cherry fruit waste.



Figure 2.3: Cross-section of coffee cherry fruit waste (Campos-Vega et al., 2015)

Massive amount of production of SCG has gained attention from the public as it may become a great pollution hazard to the environment if waste management is not done properly. The disposal of SCG into the landfill may release methane gas, which is produced by anaerobic digestion in landfill due to oxygen deficiency (Recycleuses, 2017). Methane gas is a type of greenhouse gases which will eventually lead to greenhouse effect and global warming, if its emission is not controlled. As such, there is a need to reduce SCG waste to protect the environment.

SCG is very valuable to be reutilized in industrial processes. The primary purpose is to minimise environmental impacts by making better use of these waste. One of the potential uses of SCG is bio-energy production. One of the world's largest food companies, Nestlé has proposed to utilize SCG as renewable energy source in more than 20 Nescafé factories by 2020 (Campos-Vega et al., 2015). There are some other industrial applications, such as the production of biodiesel (Caetano, Silva, & Mata, 2012), used as substrate for microorganism cultivation (Machado et al., 2012) and composting (Preethu et al., 2007). These few years, many researchers had explored the potential of SCG as low-cost bio-sorbent to remove heavy metal.

SCG is rich in lignocellulose. The structure of lignocellulose is formed by a covalently bonded network of cellulose, hemicellulose, lignin and pectin (Ballesteros, Teixeira and Mussatto, 2014; Nuruddin et al. 2016). A variety of functional groups are discovered on the SCG surface which helps in removing the heavy metal ions. For example, functional groups like amino group, carboxyl group and hydroxyl

group (Wang and Wang, 2016). This also explains why SCG has always been sought after as it is inexpensive and very effective in heavy metal removal.

A study on copper and zinc removal from wastewater was performed by Agwaramgbo, Cardoso and Matos (2017) using coffee waste as the adsorbent. The objective of the study was to evaluate the effect of adsorbent dosage on the adsorption performance, as well as the selectivity of heavy metal removal from copper-zinc binary metal mixture. The study also reported that there was high selectivity towards copper removal, while zinc removal decreased in binary metal mixture. Zinc removal was generally lower than copper removal regardless of mono or binary metal solutions. In addition, the results also indicated that high adsorbent dosage of coffee waste was more effective in heavy metal removal.

#### 2.4.2 Eggshell Waste

Egg is one of the healthiest and nutritious food in the world. It has high content of protein, which is essential for human growth. According to Department of Veterinary Services Malaysia (2015), the egg consumption per capita was 263 eggs in year 2007. In 2015, the egg consumption reached 372 eggs per year per capita in Peninsular Malaysia. Table 2.6 lists the annual egg consumption per capita from 2007 to 2015.

Table 2.6: Annual Egg Consumption Per Capita from 2007 to 2015

<b>Region</b>	<b>2007</b>	<b>2008</b>	<b>2009</b>	<b>2010</b>	<b>2011</b>	<b>2012</b>	<b>2013</b>	<b>2014</b>	<b>2015</b>
Peninsular Malaysia	263	263	283	303	309	308	319	352	372
Sabah	133	141	147	173	168	162	161	166	160
Sarawak	307	307	286	311	314	299	318	330	340

Source: Department of Veterinary Services Malaysia (2015)

According to Federation of Livestock Farmers' Associations of Malaysia, there are approximately 370 layer farms producing 12,113 million eggs in total annually. Among the layer farms, there are 6 companies which produce more than 1 million table eggs daily. Figure 2.4 presents the amount of eggs produced in different layer producing areas in Peninsular Malaysia.

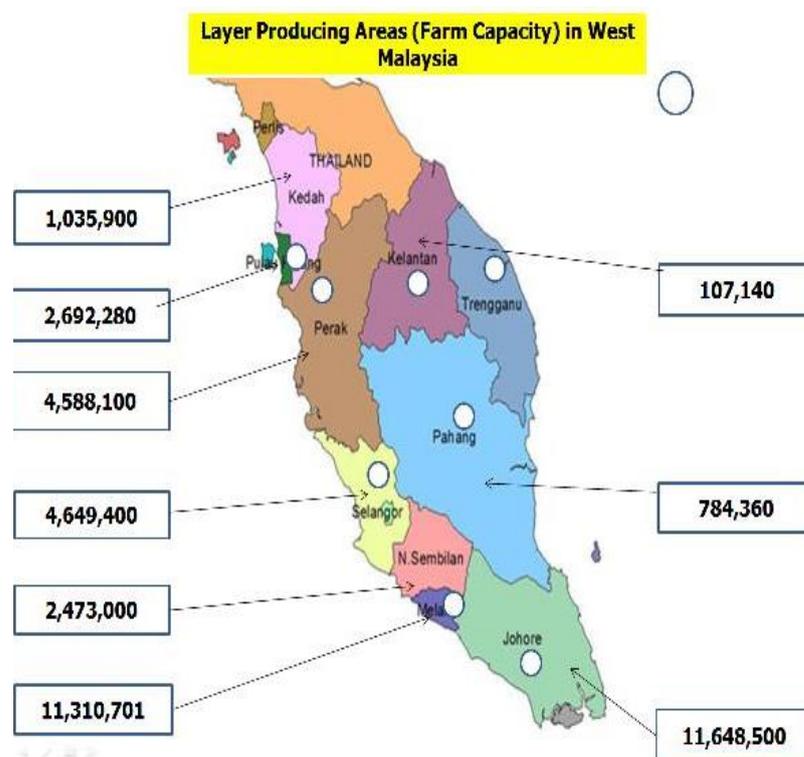


Figure 2.4: Amount of Eggs Produced in Different Layer Producing Areas in Peninsular Malaysia (Federation of Livestock Farmers' Associations of Malaysia, 2012)

Eggshell waste is made of a three-layer structured ceramic material which includes a cuticle on outer surface, spongy layer in the middle and inner lamellar layer (Tullett, 1987; Stadelman, 2000). The major composition of eggshell waste is constituted by 85-95% of calcium carbonate content which helps to adsorb heavy metal ions (Tsai et al., 2006). In addition, two eggshell membranes which reside between the eggwhite and inner surface of eggshell also helps in adsorption of metal. There is a thick outer membrane attached to the eggshell and a thin inner membrane attached to the eggwhite (Parsons, 1982; Nakano, Ikawa and Ozimek, 2003). These two membranes arrange and form a double-layered and semi-permeable membrane which consists of protein fibers.



Figure 2.5: Eggshell Waste

Eggshell waste is commonly generated in households, restaurants and bakeries. Due to high egg production and consumption, huge amount of eggshell waste is generated and it represents one of the world's worst environmental problems. Around 150,000 tons of eggshell waste are disposed in landfills in the United States per year (Toro et al., 2007). This emphasizes on the need to recycle the eggshell waste for better use, for example, used as adsorbent for heavy metal ions removal. Eggshell waste is proposed to be reused as adsorbent because it will not contribute to production of chemical sludge. Thus, it will not cause secondary pollution.

Ho et al. (2014) investigated the removal of nickel and silver ions using eggshells with membrane, eggshell membrane, and eggshells. The adsorption experiment was conducted at 45 °C and pH 5.2. . The maximum adsorption capacity of eggshells with membrane was found to be 79.1% for nickel ion using 0.2 g/20 mL adsorbent dosage. Meanwhile, the maximum adsorption capacity for silver ion was 58.0% with 100 mg/L of eggshells with membrane dosage. The optimum contact time for both nickel and silver ion adsorption was found to be 3 hours.

Another study was batch scale adsorption experiment conducted by Chavan and Mane (2015) using chicken eggshells as adsorbent to remove copper and zinc ions from water. The optimum pH for copper and zinc ions removal was reported as pH 6. The optimum contact time was 2 hours with agitation speed of 170 rpm. The study also proved that adsorption performance was enhanced by increasing adsorbent dosage.

### 2.4.3 Papaya Seed

Papaya is a rich source of antioxidant nutrients, B vitamins, minerals and fiber. It is also a source of digestive enzyme papain, which is utilized in many industries such as beauty products, brewing, cosmetics, meat tenderizing and pharmaceuticals (Evans and Ballen, 2012). Thus, papaya is an essential fruit which provides vitamins and nutrients for human health.

Papaya is a tropical fruit crop of Malaysia, which is produced in abundance up to 72000 tonnes per year (Hameed, 2009). In 2016, papaya was named as the fruit which had the highest self-sufficiency ratio (SSR) in Malaysia. Table 2.7 depicts the SSR of the top 5 fruits which recorded the highest SSR in Malaysia in 2016.

Table 2.7: Self-sufficiency Ratio of Agricultural Commodities (Fruits) Malaysia in 2016

<b>Fruits</b>	<b>SSR (%)</b>
Papaya	158.7
Watermelon	153.6
Starfruit	140.1
Mangosteen	113.4
Jackfruit	108.8

Source: Department of Statistics Malaysia (2016)

Solid wastes like papaya peels or seeds are always disposed and papaya seeds constituted 15-20% of the weight of papaya (Hameed, 2009). High production and consumption of papaya fruit will generate enormous amount of papaya seeds waste, which is disposed in the landfill eventually. To prevent environmental problem caused by the accumulation of waste, papaya seeds is proposed as agro-waste adsorbent for the adsorption of heavy metal.



Figure 2.6: Papaya fruit

The primary constituents of papaya seed are cellulose and lignin. Lignin is a macromolecule which comprises of many polar functional groups which are helps to remove heavy metal ions. For instance, functional groups such as alcohol, aldehydes, carboxyl, ether, ketone and phenol group (Saikaew, Kaewsarn and Saikaew, 2009).

In the past, there were some researches and reviews on the adsorption performance of papaya seed. Abd. Hadi, Rohaizar and Wong (2011) investigated the removal of copper ions from aqueous solution using papaya seed. The effect of pH and stirring speed was observed on the removal of copper ions. The optimum conditions for copper adsorption were pH 6 and 350 rpm to yield the maximum adsorption capacity of 212 mg/g. The equilibrium data followed the Langmuir adsorption isotherm and the adsorption kinetics data was well-described by the pseudo-second-order kinetic model.

Another study conducted by Chithra, Lakshmi and Jain (2014) investigated the bio-sorption potential of papaya seed on the adsorption of nickel and chromium ions from aqueous solution. The study was performed in batch mode by varying the initial pH, bio-sorbent dosage, initial metal ions concentration and temperature. The results indicated pH 6 with bio-sorbent dosage of 1.0g/100 mL was the optimum condition for nickel ion to achieve maximum adsorption performance. Meanwhile, for chromium ion, pH 2 with bio-sorbent dosage of 0.4 g/100 mL was the best condition. The adsorption capacities of papaya seed for nickel and chromium ions were 5.58 and 5.85 mg/g, respectively.

## 2.5 Adsorption Isotherm Models

Adsorption isotherm is imperative for better understanding of adsorption process and improvement of adsorption system design (El-Khaiary, 2008). It is often applied to observe the interaction between the adsorbent and the adsorbate. The adsorption isotherm models can be used to express the adsorption equilibrium data. The most frequently used adsorption isotherm models are Langmuir and Freundlich models as these models are simple and explicit. The relationship between the amount of adsorbed solute and the solute concentration of the adsorbate is expressed by fitting the adsorption equilibrium data into Langmuir and Freundlich adsorption isotherm equations.

### 2.5.1 Langmuir Adsorption Isotherm

Langmuir adsorption describes the chemical, physical or physiochemical interaction between the solid particles and empty sites of the adsorbent surface. It is usually applied to contrast the adsorption capacity of different adsorbents by balancing the relative adsorption and desorption rates to achieve dynamic equilibrium. There are three basic assumptions of Langmuir isotherm. Firstly, Langmuir isotherm equation is only based on monolayer sorption onto specific sites of a surface (Iqbal, Saeed and Kalim, 2009). Secondly, the surface sites of the adsorbent are all similar and can only bind to one atom each. Thirdly, the occupancy of neighbouring sites on the adsorbent has no influence on the ability of a molecule to be adsorbed (Zhao et al., 2011). The Langmuir equation is presented in Equation (2.1):

$$Q_e = \frac{Q_{max}K_L C_e}{1 + K_L C_e} \quad (2.1)$$

where

$Q_e$  = amount of adsorbent adsorbed at equilibrium, mg/g

$C_e$  = concentration of solute after reaching equilibrium, mg/L

$Q_{max}$  = maximum adsorption capacity, mg/g

$K_L$  = adsorption energy, L/mg

### 2.5.2 Freundlich Adsorption Isotherm

Freundlich adsorption makes assumption that the adsorbent has a highly heterogeneous surface. Therefore, the binding sites of the adsorbent are not identical. Even though Freundlich isotherm is often being used, it does not have information on monolayer adsorption capacity, if compared to the Langmuir model (Aksu and Ferda, 2003; Yu et al., 2000; Ferda and Selen, 2012). Freundlich isotherm equation for single component adsorption is expressed in Equation (2.2) (Azouaou et al., 2010):

$$Q_e = kC_e^{\frac{1}{n}} \quad (2.2)$$

where

$Q_e$  = amount of adsorbent adsorbed at equilibrium, mg/g

$C_e$  = concentration of solute after reaching equilibrium, mg/L

$k$  = Freundlich constant representing the adsorption capacity

$n$  = Freundlich constant representing the adsorption intensity

### 2.6 Adsorption Kinetics Models

Kinetic studies are usually conducted to estimate on the optimum working condition of commercial batch adsorption processes (Febrianto et al., 2009). Kinetic models namely pseudo-first-order and pseudo-second-order kinetic models are frequently employed to explore the adsorption kinetics and measure the extent of uptake in certain adsorption kinetics. However, the applications of adsorption kinetic models are only for assumptions. It does not represent the real adsorption process. The mechanisms of adsorption and possible rate-limiting steps like chemical reaction processes or mass transport are described and identified through the kinetic models (Febrianto et al., 2009; Park, Yun and Park, 2010; Kyzas, Fu and Matis, 2014).

Pseudo-first-order kinetic model was first suggested by Lagergren at late 19<sup>th</sup> century. This model stated that the adsorption process is limited by diffusion process (Rudzinski and Plazinski, 2007). Meanwhile, pseudo-second-order kinetic model was later introduced in the mid 80's (Blanchard, Maunaye and Martin, 1984; Gosset, Trancart and Thévenot, 1986). This model made assumption that the adsorption process was limited by the adsorption reaction occurred at liquid-solid interface of

the adsorbent (Pignatello and Xing, 1995). The equations for pseudo-first-order and pseudo-second-order kinetic models were presented in Equations (3.4) and (3.5).

## CHAPTER 3

### METHODOLOGY AND WORK PLAN

#### 3.1 Preparation of Synthetic Wastewater

One thousand mg/L of copper and nickel single-metal stock solutions were prepared by dissolving copper sulphate metal salts,  $\text{CuSO}_4$  and nickel sulphate metal salts,  $\text{NiSO}_4$  in 100 mL of deionised water and further diluted in 1000 mL volumetric flask, respectively. Twelve mg/L of copper solution and 6 mg/L of nickel solution were mixed in 1:1 volume ratio according to the industrial limit for 10 minutes to form a binary-metal solution (Agwaramgbo, Cardoso and Matos, 2017).

#### 3.2 Preparation of Adsorbents

In this study, SCG, eggshell waste and papaya seeds were used to prepare the adsorbents. The SCG were collected from cafes in Sg. Long and washed thoroughly with deionized water until the water becomes colourless. After that, the SCG were dried in an oven at 60 °C for 24 hours to ensure all the moisture was removed (Lafi et al., 2014). The SCG were then crushed into smaller pieces with grinder and sieved to particle size < 850  $\mu\text{m}$ . The dried SCG were then kept in plastic container with lid for further use.

Eggshells were collected from the bakery shop in Sg. Long. The eggshells were washed thoroughly using deionized water to get rid of dirt. After that, the eggshells were dried in an oven at 40 °C for 24 hours (Rohaizar, Hadi and Wong, 2013). The dried eggshells were ground into powder form, sieved to particle size < 850  $\mu\text{m}$  and then kept in plastic container with lid for further use.

Papaya seeds were collected from fruit stalls in Sg. Long. The papaya seeds were washed thoroughly using deionized water. Then, the seeds were boiled for 20 minutes to break and filter out the papaya seed coat (Chithra, Lakshmi and Jain, 2014). Subsequently, the seeds were dried in an oven at 60 °C for 24 hours. The dried seeds were then crushed into powder form with grinder and sieved to particle size < 850  $\mu\text{m}$ . The papaya seed powder was kept in plastic container with lid for further use.

### 3.3 Characterisation of Adsorbents and Synthetic Wastewater

Table 3.1 shows the different equipment used for the characterisation of adsorbent and synthetic wastewater before and after adsorption.

Table 3.1: Equipment used for characterisation of adsorbent and synthetic wastewater

<b>Equipment</b>	<b>Model</b>
Scanning Electron Microscopy (SEM)	Hitachi SEM Model S-3400N
Fourier-Transform Infrared Spectroscopy (FTIR)	Thermo Scientific Nicolet iS10
Spectrophotometer	Hach DR-3900
pH meter	Eutech PC 300
Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)	Perkin Elmer Optima 7000

#### 3.3.1 SEM

SEM (Hitachi SEM Model S-3400N) analysis was used to investigate the morphologies of the adsorbent surface before and after adsorption. Prior to the analysis, the samples were prepared by adhering on the specimen holder using double-sided tape. Then, the samples surfaces were coated with a layer of platinum or gold by sputter coater to make them conductive. The SEM analysis was conducted at voltage of 15 kV to examine the surface structure of the samples. The SEM images of the samples were collected at different magnifications from 300x to 2.10kx to observe the differences in surface morphologies.

#### 3.3.2 FTIR

FTIR (Thermo Scientific Nicolet iS10) analysis was conducted for detection of functional groups of adsorbents which helped in removing copper and nickel ions. Firstly, the sample holder was cleaned with alcohol to ensure it was free from impurities to collect the background data. Then, a small amount of samples was loaded onto the holder to perform FTIR analysis.

### **3.3.3 Spectrophotometer**

The copper ion concentrations in synthetic wastewater before and after adsorption was tested with the spectrophotometer (Hach DR-3900) according to Hach Bicinchoninate Method 8506. The method started by filling the first sample cell with 10 mL of copper solution after filtering the adsorbents. Then, the sample cell was added with CuVer 1 Copper Reagent powder pillow and swirled to mix for 2 min. Meanwhile, another sample cell was filled with 10 mL of copper solution as blank. The blank solution was first inserted into the cell holder to zero the reading. After that, the sample cell containing mixture of CuVer reagent and copper solution was inserted and the final reading of copper ion concentration was displayed.

### **3.3.4 ICP-OES**

The concentration of nickel ion was tested using ICP-OES (Perkin Elmer Optima 7000). Standard solutions of 2, 4, 6, 8, 10 and 12 mg/L were prepared to obtain a calibration standard curve prior to the analysis. After that, the nickel solutions after adsorption were tested using ICP-OES.

### **3.3.5 pH Meter**

The pH level of the synthetic wastewater was measured using pH meter (Eutech PC 300) after micro-addition of HCl or NaOH.

## **3.4 Parameter Study**

Several parameters were studied in this experiment, namely pH, initial metal concentration, adsorbent dosage and contact time. The adsorption experiment was performed in batch mode.

### **3.4.1 Effect of pH**

The effect of pH on adsorption performance was carried out by mixing 3 g of SCG, papaya seed powder and eggshell powder with 12 mg/L of copper solution, at a range of pH (value of 3, 4.5, 6, 7.5, 9). The desired pH value was adjusted by adding little amount of either 0.1 M HCl or 0.1 M NaOH. Then, the pH was measured with pH meter (Eutech PC300). All the samples were agitated with orbital shaker for 1 hr.

Similar procedure was repeated for Ni (II) adsorption with 6 mg/L of Ni (II) single-metal stock solution.

#### **3.4.2 Effect of Initial Metal Concentration**

The effect of initial metal concentration was performed by changing the initial single-metal concentration (4, 6, 8, 10, 12 mg/L) of copper and nickel. Different initial metal concentrations were mixed with 3 g of adsorbents and the adsorption experiment was performed at pH 4 under agitation for 1 hr.

#### **3.4.3 Effect of Adsorbent Dosage**

SCG, papaya seed powder and eggshell powder at amount of 2, 4, 6, 8 and 10 g were mixed with 12 mg/L of initial single-metal concentrations of copper. The adsorption experiment was performed at pH 4 under agitation for 1 hr. The same procedure was repeated for nickel adsorption with 6 mg/L of nickel single-metal stock solution.

#### **3.4.4 Effect of Contact Time**

The effect of contact time on adsorption performance was carried out by mixing 6 g of SCG, papaya seed powder and eggshell powder with 12 mg/L of 300 mL single-metal stock solution of Cu (II). The agitation was conducted at pH 4 using magnetic stirrer for 90 min. The metal solution was first collected at fixed intervals of 2.5 min until the 10th min, then at intervals of 5 min until the 30th min and finally at intervals of 30 min for chemical analysis. Same procedure was repeated for Ni (II) adsorption with 6 mg/L of Ni (II) single-metal stock solution.

#### **3.5 Selectivity Study**

The selectivity of SCG, papaya seed powder and eggshell powder towards the removal of copper and nickel ions from binary-metals synthetic wastewater was also investigated. The adsorption experiment was carried out by agitating 3 g of various adsorbents with binary-metals solution of pH 4 for 1 hr. Comparison was then made among the adsorption of single copper solution, single nickel solution and binary Cu-Ni solution. The selectivity of metal ion adsorption was determined by measuring the percentage removal of copper and nickel ions to show which metal ion had higher

affinity to the adsorbents. The selectivity study was only conducted once due to time constraint.

### 3.6 Isotherms Study

After conducting batch adsorption, the adsorption data was fitted into Langmuir and Freundlich isotherms. The metal ions removal was determined using Equation (3.1).

$$Q_e = \frac{(C_o - C_e)V}{m} \quad (3.1)$$

where

$Q_e$  = amount of metal ions removal at equilibrium, mg/g

$C_o$  = initial concentration of metal ion in liquid sample, mg/L

$C_e$  = equilibrium concentration of metal ion in liquid sample, mg/L

$V$  = volume of liquid sample, L

$m$  = mass of adsorbent, mg

For Langmuir isotherm, the  $C_e$  and  $Q_e$  obtained from Equation (3.1) were fitted into the linearized Langmuir equation:

$$\frac{C_e}{Q_e} = \left( \frac{C_e}{Q_{max}} \right) + \frac{1}{(K_L Q_{max})} \quad (3.2)$$

where

$Q_{max}$  = maximum adsorption capacity, mg/g

$K_L$  = adsorption energy, L/mg

A graph of  $\frac{C_e}{Q_e}$  against  $C_e$  was plotted. The slope of the graph could be used to find the  $Q_{max}$  and the intercept could be used to find  $K_L$ . Meanwhile, for Freundlich isotherm, the  $C_e$  and  $Q_e$  obtained from Equation (3.1) could also be fitted into the linearized Freundlich isotherm equation:

$$\log Q_e = \log K_F + \left( \frac{1}{n} \right) \log C_e \quad (3.3)$$

where

$K_F$  = Freundlich constant representing the adsorption capacity

$n$  = Freundlich constant representing the adsorption intensity

A graph of  $\log Q_e$  against  $\log C_e$  was plotted. The slope of the graph could be used to find  $1/n$  and the intercept could be used to find  $K_F$ .

### 3.7 Kinetics Study

The kinetics data obtained at fixed time intervals were fitted into the pseudo-first-order, Equation (3.4) and pseudo-second-order, Equation (3.5).

$$\log(Q_e - Q_t) = \log(Q_e) - \frac{k_1}{2.303} t \quad (3.4)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \left(\frac{1}{Q_e}\right) t \quad (3.5)$$

where

$Q_e$  = amount of metal ions adsorbed at equilibrium, mg/g

$Q_t$  = amount of metal ions adsorbed at any time  $t$ , mg/g

$k_1$  = rate constant of pseudo-first-order equation,  $\text{min}^{-1}$

$k_2$  = rate constant of pseudo-second-order equation,  $\text{min}^{-1}$

For pseudo-first-order equation, a straight-line plot of  $\log(Q_e - Q_t)$  against  $t$  was plotted. The slope gave the  $Q_e$ , while the intercept gave  $k_1$ . For pseudo-second-order equation,  $\frac{t}{Q_t}$  was plotted against  $t$ . The slope and intercept would give  $Q_e$  and  $k_2$ , respectively.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Characterisation of Adsorbents

The physiochemical properties of SCG, eggshell powder and papaya seeds powder were characterised using FTIR and SEM. SEM was required to observe the morphology of the adsorbents before and after adsorption. Meanwhile, FTIR was needed to identify the presence of functional groups on the adsorbent surface which helped to remove Cu (II) and Ni (II) metal ions.

##### 4.1.1 SEM

Figures 4.1-4.3 showed the surface morphology of SCG, eggshell powder and papaya seeds powder before and after adsorption of Cu (II) and Ni (II) single-metal solutions and Cu-Ni binary-metals solution.

Based on Figure 4.1, it was clearly observed that there was no significant difference between the surface morphology before and after adsorption as modification of SCG was not performed. The surface of SCG seemed rough and contained abundant flaky protuberances (Hao, Wang and Valiyaveetil, 2017). This also implied that the adsorption experiments did not improve the surface morphology of SCG as the SCG surface remained unsmooth and irregular after adsorption. Different sizes of cavities were found on the surface, which could be assumed as channels for the adsorption of Cu (II) and Ni (II) ions onto the SCG surface (Oliveira et al., 2008; Kyzas, Lazaridis and Mitropoulos, 2012). These cavities indicated high accessibility to the SCG pore network as well as higher cross-sectional area for surface adsorption (Futalan, Kim and Yee, 2019). Hence, the reuse potential of SCG as adsorbent for elimination of heavy metal ions was proven.

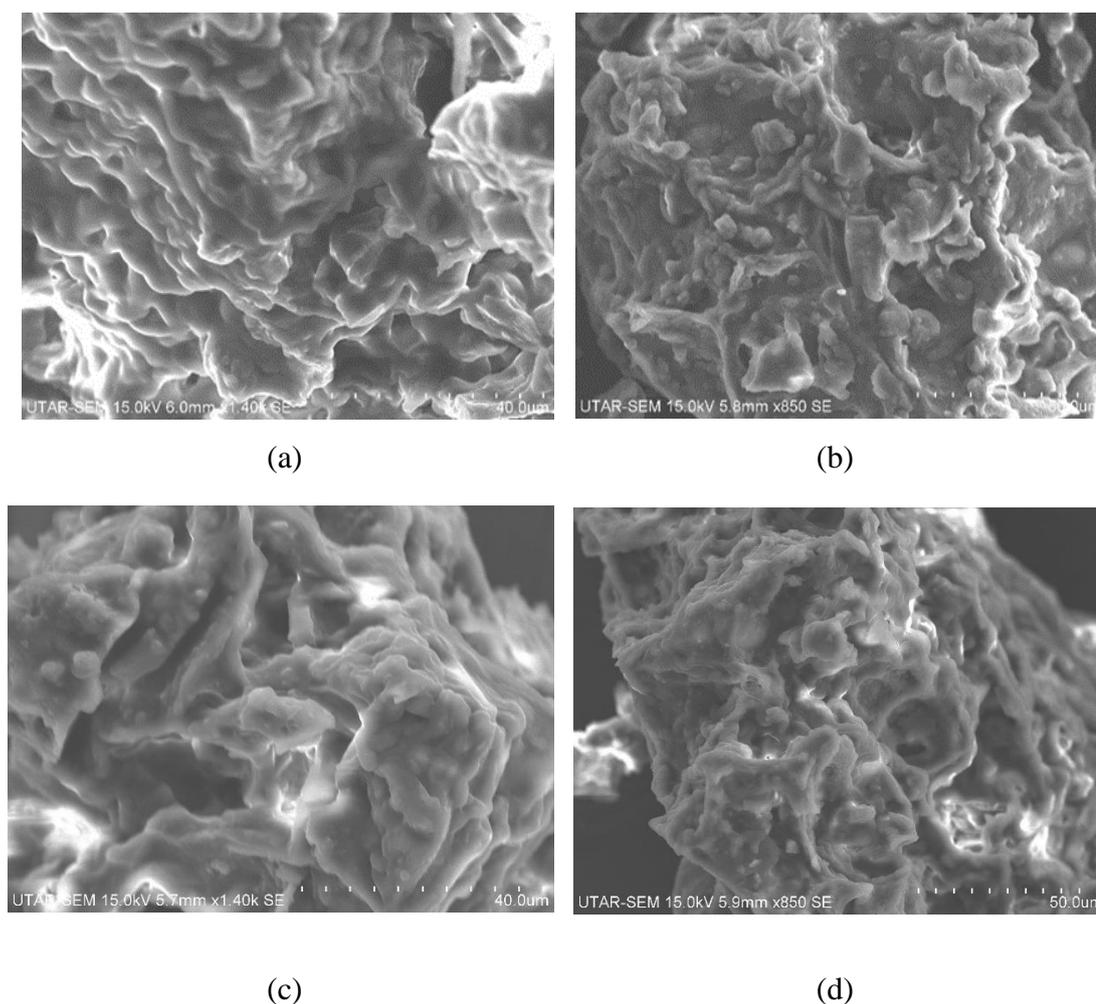


Figure 4.1: SEM Images for SCG (a) Before Adsorption (b) After Cu (II) Adsorption (c) After Ni (II) Adsorption (d) After Cu-Ni Adsorption

Figures 4.2a and 4.2c demonstrated the macroporous network structure of surface of eggshell powder (Wang et al., 2008). Intertwined and coalescing fibers were observed obviously on the adsorbent surface (Wang et al., 2008). The membrane fibers indicated the presence of calcium carbonate which enhanced the adsorption of heavy metal ions. Figures 4.2b and 4.2d depicted angular pattern of fractures on adsorbent surface owing to the crystalline structure of eggshell particles (Tsai et al., 2006). The surface was observed to be not smooth and irregular. In addition, the blisters on the surface showed the presence of vesicular holes within the palisade layer of eggshell for Figures 4.2b and 4.2d (La Scala Jr et al., 2000). However, the membrane fibers in Figures 4.2b and 4.2d were not as obvious as in Figures 4.2a and 4.2c. In short, eggshell powder proved its efficiency in heavy metal

ions removal as it was made of a porous structure with numerous membrane fibers, which undoubtedly helped in adsorption of heavy metal ions.

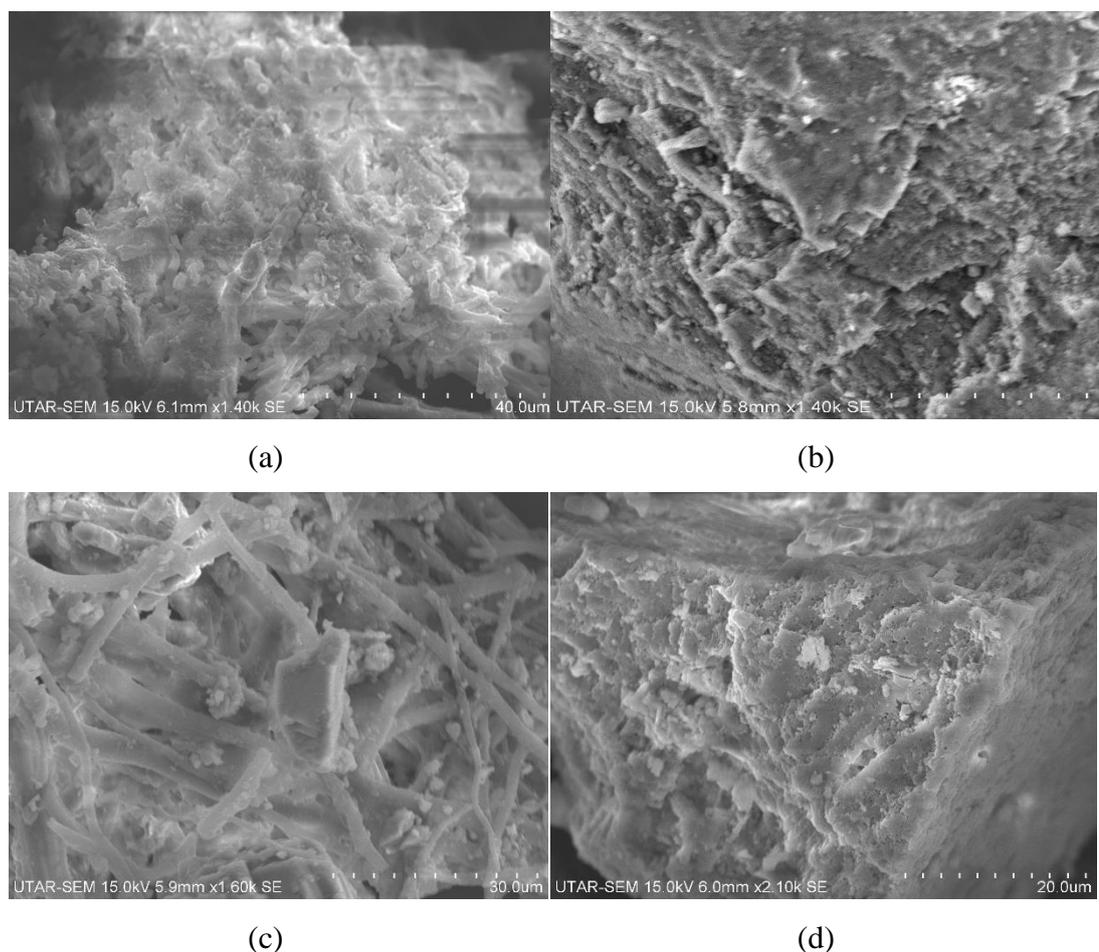


Figure 4.2: SEM Images for Eggshell Powder (a) Before Adsorption (b) After Cu (II) Adsorption (c) After Ni (II) Adsorption (d) After Cu-Ni Adsorption

Figures 4.3a and 4.3b exhibited heterogeneous, irregular and rough surfaces similar to the SCG (Yenisoy-Karakaş et al., 2004). Meanwhile, Figures 4.3c and 4.3d illustrated the honeycomb network structure of pores of the papaya seeds powder surface. The pore evolution occurred due to the volatile compounds trapped inside the particles were forced to diffuse out. The volatiles were formed by non-carbonic elements, namely oxygen and hydrogen during decomposition (Raveendran and Ganesh, 1997). The porous structure presented in Figure 4.3 evidently showed that papaya seeds powder had the potential to be reused for adsorption process.

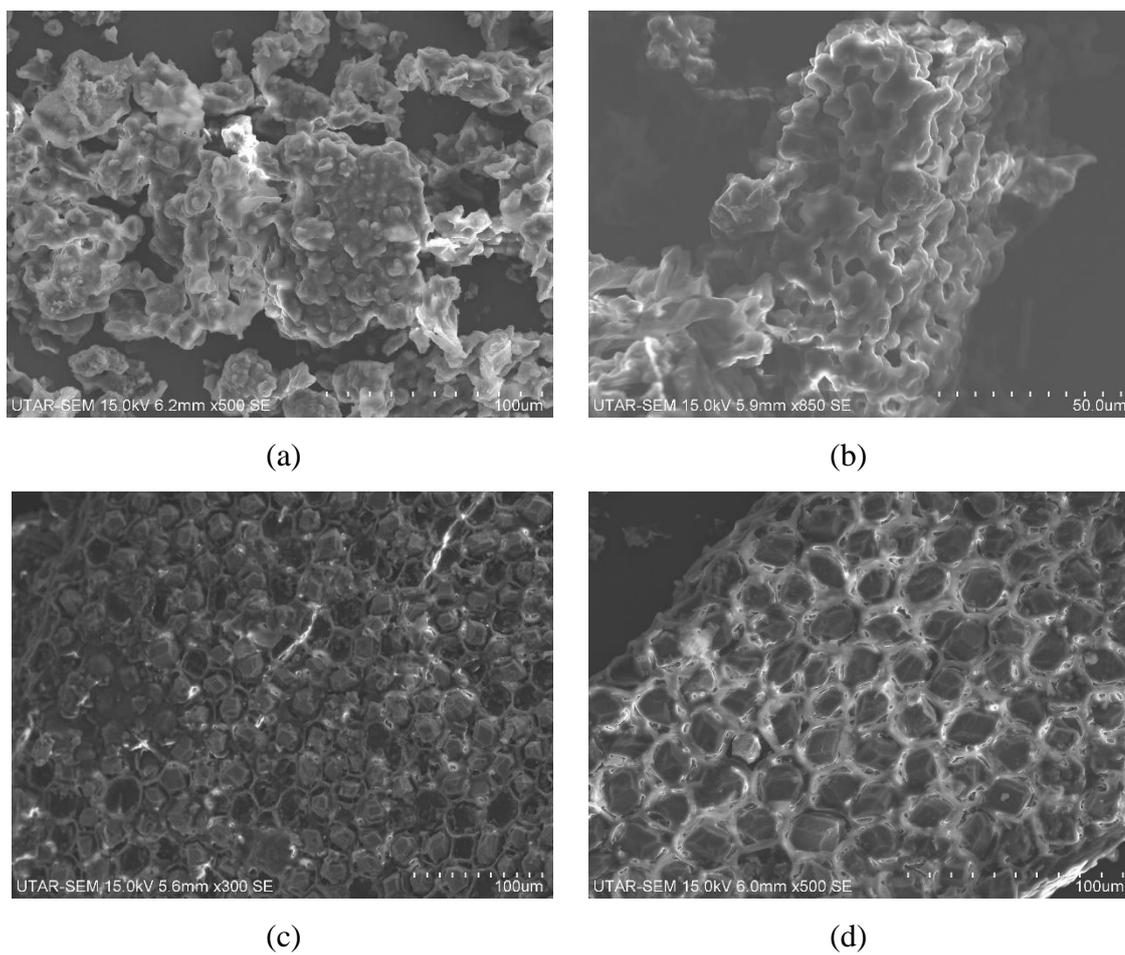


Figure 4.3: SEM Images for Papaya Seeds Powder (a) Before Adsorption (b) After Cu (II) Adsorption (c) After Ni (II) Adsorption (d) After Cu-Ni Adsorption

#### 4.1.2 FTIR

Figures 4.3-4.5 depicted the FTIR spectrum images of SCG, eggshell powder and papaya seed powder before adsorption and after adsorption in single Cu, single Ni and Cu-Ni binary-metals solutions.

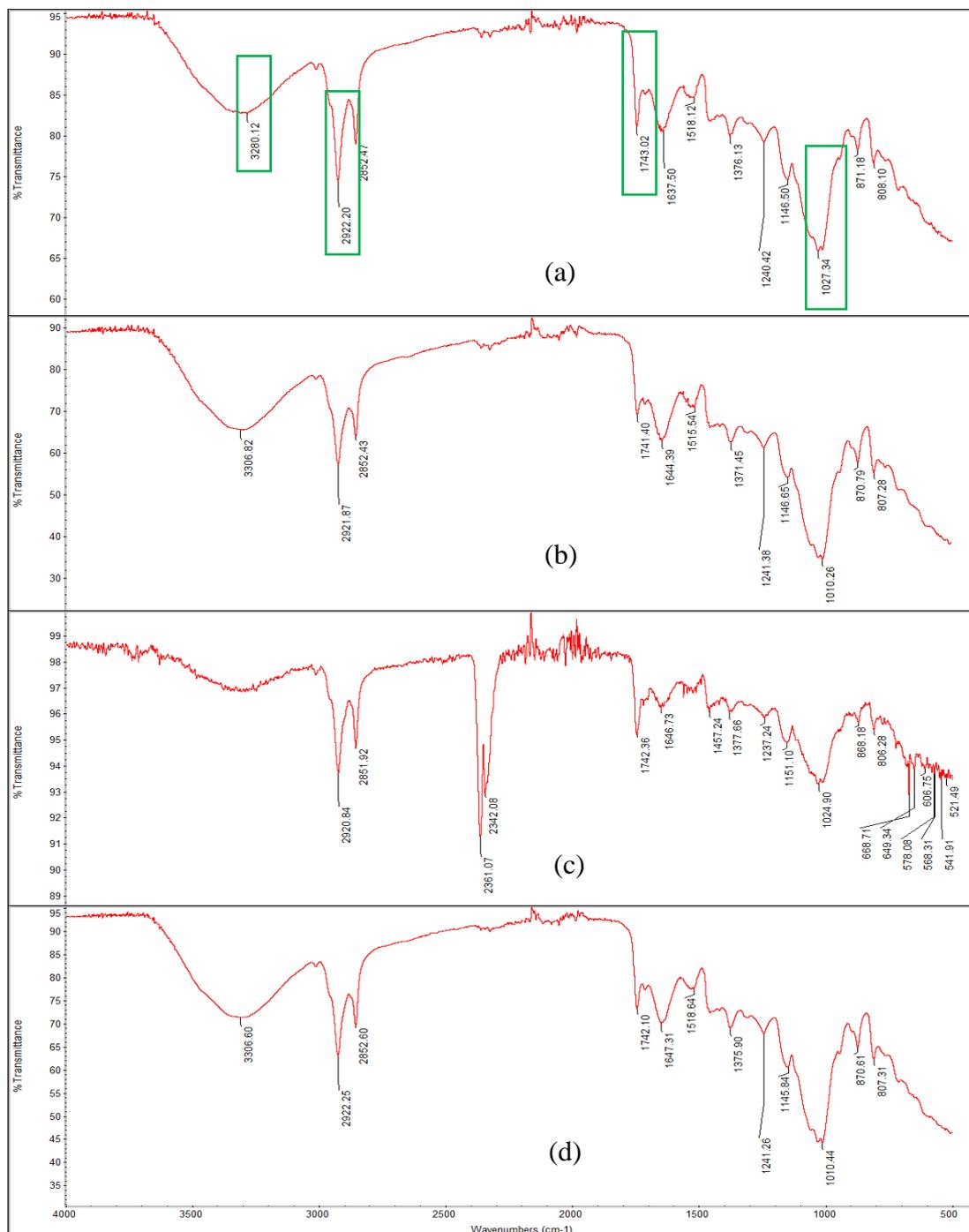


Figure 4.4: FTIR Spectrum Images of SCG (a) Before Adsorption (b) After Cu Adsorption (c) After Ni (II) Adsorption (d) After Cu-Ni Adsorption

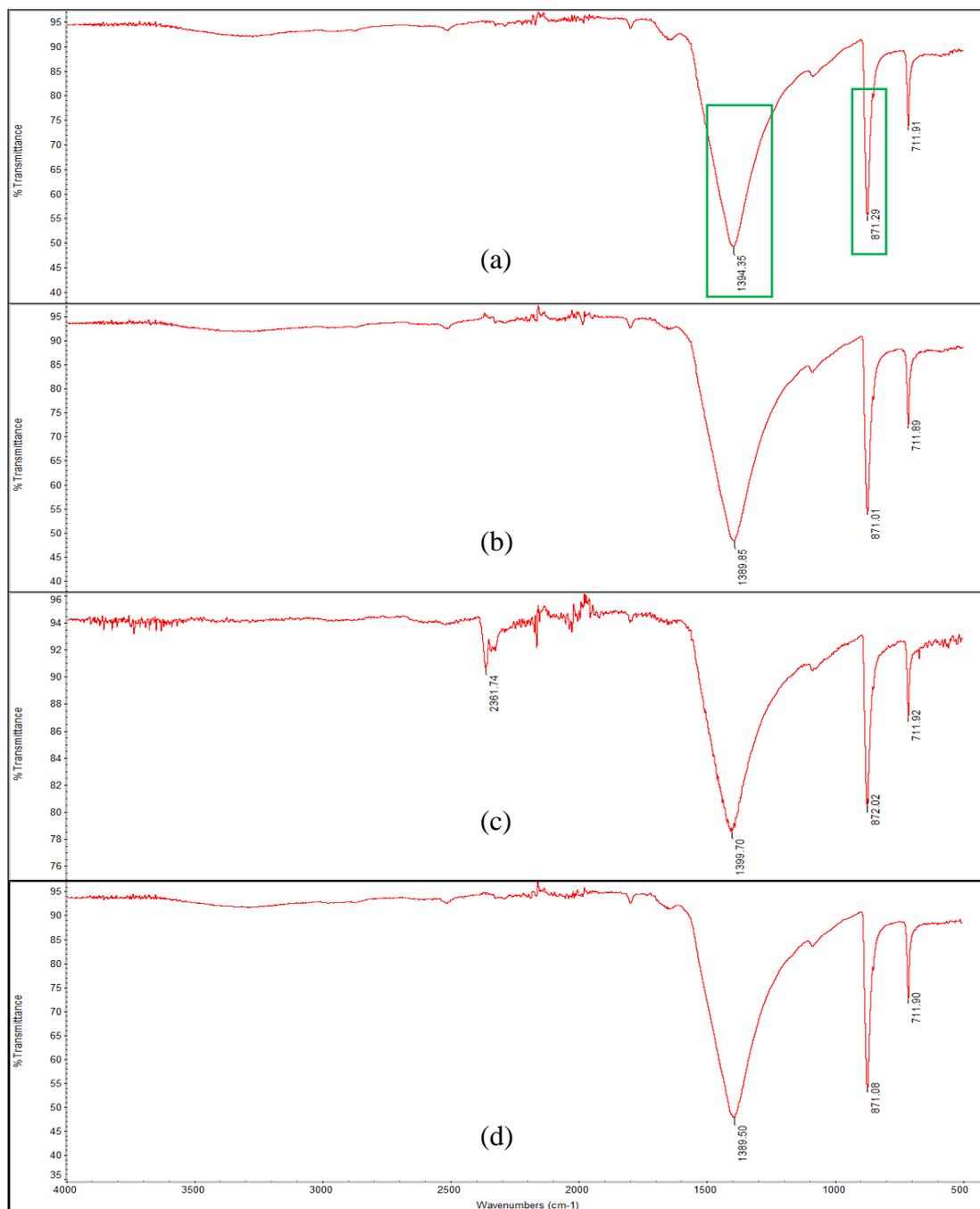


Figure 4.5: FTIR Spectrum Images of Eggshell Powder (a) Before Adsorption (b) After Cu Adsorption (c) After Ni (II) Adsorption (d) After Cu-Ni Adsorption

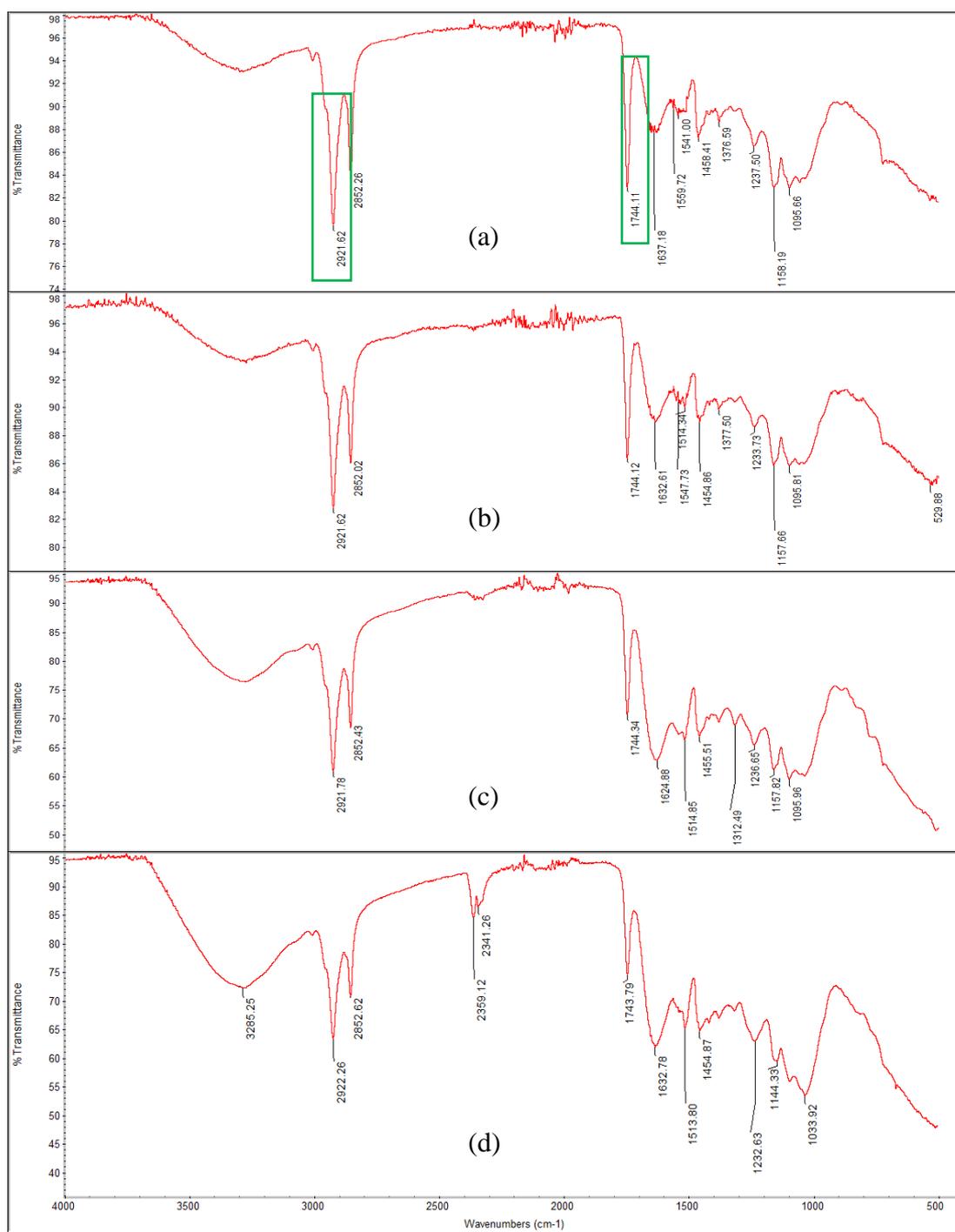


Figure 4.6: FTIR Spectrum Images of Papaya Seed Powder (a) Before Adsorption (b) After Cu Adsorption (c) After Ni (II) Adsorption (d) After Cu-Ni Adsorption

Table 4.1: Interactions of Functional Groups of SCG, Eggshell Powder and Papaya Seed Powder and Their Shifts in FTIR Spectra

Adsorbent	Compound Class	Functional Group	Wavelength (cm <sup>-1</sup> )	
			Before Adsorption	After Adsorption
<b>SCG</b>	Amine	C-N Stretching	1027.34	1010.44 (Cu)
				1024.90 (Ni)
				1010.26 (Cu+Ni)
	Esters	C=O Stretching	1743.02	1741.40 (Cu)
				1742.36 (Ni)
				1742.10 (Cu+Ni)
Alkane	C-H Stretching	2922.20	2922.25 (Cu)	
			2920.84 (Ni)	
			2921.87 (Cu+Ni)	
Alcohol	O-H Stretching	3280.12	3306.83 (Cu)	
			3306.60 (Cu+Ni)	
<b>Eggshell Powder</b>	1,2- disubstituted or 1,2,3- trisubstituted	C-H Bending	871.29	871.01 (Cu)
				872.02 (Ni)
				871.08 (Cu+Ni)
Sulfate	S=O Stretching	1394.35	1389.85 (Cu)	
			1399.70 (Ni)	
			1389.50 (Cu+Ni)	
<b>Papaya Seed Powder</b>	Alkane	C-H Stretching	2921.62	2921.62 (Cu)
				2921.78 (Ni)
				2922.26 (Cu+Ni)
Esters	C=O Stretching	1744.11	1744.12 (Cu)	
			1744.34 (Ni)	
			1743.79 (Cu+Ni)	

Source: Sigma-Aldrich (n.d.)

Table 4.1 presents the functional groups identified in SCG, eggshell powder and papaya seed powder as well as the shifting of adsorption wavenumber before and after adsorption. The shifting of wavenumber indicated that metal binding process occurred on the adsorbent surface (Naiya, Singha and Das, 2011).

For SCG, the presence of amine, esters, alkane and alcohol group was discovered. An obvious shift was noticed from 1027.34 to 1010.44  $\text{cm}^{-1}$  and 1010.26  $\text{cm}^{-1}$  for single copper and Cu-Ni binary-metals solutions, which was referred to the C-N stretching vibration. This proved that the stretching of C-N group was responsible for the adsorption of Cu (II) ions. The FTIR spectrum of SCG also displayed that there was a major shift of peak from 3280.12  $\text{cm}^{-1}$ , which was referred to the O-H stretching, to 3306.83 and 3306.60  $\text{cm}^{-1}$  for single copper and Cu-Ni binary-metals solutions. Similarly, it was evident that the OH group was useful in Cu (II) adsorption. However, there was no peak found in correlation to the wavenumber 3306.83  $\text{cm}^{-1}$  in single nickel adsorption. This could be ascribed to a different interaction occurring between Ni (II) and the O-H group on SCG surface (Al Lafi and Al Abdullah, 2015). The adsorption of ions on the binding sites was affected by their ionic radii. Larger ionic radii metal ions would be attached on the adsorbent surface, whereas smaller metal ions would be adsorbed into the adsorbent (Al Lafi and Al Abdullah, 2015).

For eggshell powder, only minor shift of peak was observed and the functional groups responsible for adsorption were C-H bending and S=O stretching vibration. The results revealed that there was interaction between the functional groups and metal ions, but it did not clearly depict the affinity of functional groups of the eggshell powder towards metal ions. Similarly, papaya seed powder also had minor shifts of peak and the functional groups involved in adsorption were C-H and C=O groups.

## 4.2 Parameter Study

Adsorption experiment was conducted on different parameters to determine the percentage removal of metal ions and evaluate the adsorption capacity of different adsorbents. The optimum experimental conditions and the affinity of adsorbents towards certain metal ions were further discussed.

### 4.2.1 Effect of pH

pH of solution was one of the utmost important factors which greatly affects the adsorption of heavy metal ions. Changes in pH would affect the surface charge of the adsorbent, the ionization degree of adsorbate and some adsorbate specification (Mayur and Sachin, 2015). Figure 4.7 illustrated the effect of pH ranging from 3 to 9 on the percentage removal of Cu (II) ions for SCG, papaya seed powder and eggshell powder.

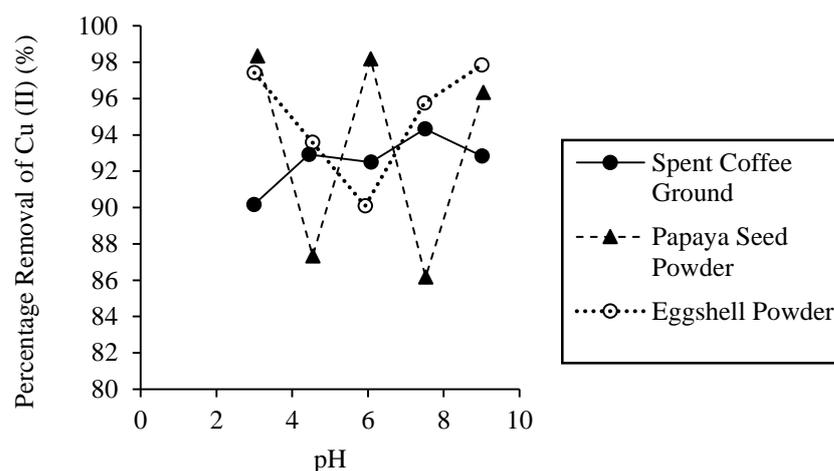


Figure 4.7: Effect of pH on The Percentage Removal of Cu (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

From Figure 4.7, it was clearly seen that SCG achieved generally lower adsorption than papaya seed powder and eggshell powder. At pH 3, SCG achieved the least percentage removal of Cu (II) ions. This could be associated with the presence of abundant hydrogen ions in copper sulphate solution at acidic pH. More acidic solution resulted in higher concentration of hydrogen ions as hydrochloric acid was more readily to dissociate into hydrogen ions (Khan Academy, n.d.). The hydrogen ions competed with Cu (II) ions for the adsorption sites on SCG, and thus leading to lower adsorption of Cu (II) ions (Thilagan, Gopalakrishnan and Kannadasan, 2013). Another reason which could be ascribed to lower Cu (II) adsorption of Cu (II) at acidic pH was the solubility of heavy metal ions at low pH. According to Reddy, Wang and Gloss (1995), the solubility of heavy metal ions like Cu (II) increased when pH decreased, which would cause toxicity and contamination

issues. The Cu (II) ions were assumed to have been dissolved in the solution instead of being removed. As a result, lower percentage removal of Cu (II) was obtained.

Subsequently, the Cu (II) ions removal percentage rose steadily with pH and eventually reached maximum adsorption at pH 7.5. This might be due to lower concentration of hydrogen ions as pH increased. In addition, ample negatively charged ligands of SCG reacting with Cu (II) ions also enhanced the heavy metal ions removal (Kyzas, 2012). However, as pH value exceeded pH 7.5, adsorption rate became lower. At high pH, Cu (II) ions would precipitate as copper hydroxide which decreased the adsorption of Cu (II) ions (Nuhoglu and Oguz, 2003; Mohan, Singh and Singh, 2005).

For eggshell powder, Figure 4.7 depicted an entirely different trend from SCG, in which the percentage removal of Cu (II) decreased at acidic pH range and followed by an increase in removal at alkaline pH. The decline in adsorption performance could be inferred that the surface charge of eggshell powder was altered by the pH of solution, becoming more positively charged. Thus, less Cu (II) was adsorbed due to electrostatic repulsive force between like charges (Zuorro et al., 2013). As the solution became more alkaline, the sodium hydroxide added into the solution might dissociate completely to produce hydroxide ions, which would then absorb the active hydrogen ions (Khan Academy, n.d.). Hence, it lowered the competition between hydrogen ions and Cu (II) ions, which allowed more Cu (II) ions to attach onto the adsorbent active binding sites. Highest Cu (II) ions percentage removal was obtained at pH 9.

Meanwhile, there was no specific trend in the percentage removal of papaya seed powder at different pH values. This might be due to different chemical structure of adsorbent and change in surface charge affected by solution pH (Kyzas, 2012). However, it was evident that SCG displayed better chemical stability compared to the other two adsorbents, despite of achieving removal percentage as high as 98%.

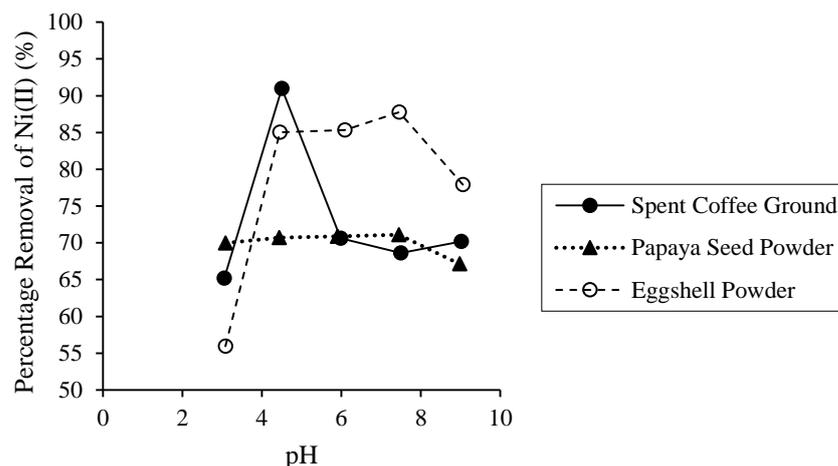


Figure 4.8: Effect of pH on The Percentage Removal of Ni (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

Figure 4.8 depicted the impact of pH on adsorption for Ni (II) ions by SCG, papaya seed powder and eggshell powder. Both SCG and eggshell powder achieved the lowest percentage removal of Ni (II) at pH 3. A possible explanation could be due to the strong electrostatic repulsive force between positively charged surface of the adsorbents and the Ni (II) ions, and thus restraining Ni (II) ions from binding to the adsorption sites (Zhang and Wang, 2015). Subsequently, the percentage removal of Ni (II) using SCG and eggshell powder increased drastically from pH 3 to 4.5. This was because the repulsive force decreased with increasing pH, and hence the Ni (II) adsorption increased (Zhang and Wang, 2015). The adsorption by eggshell powder remained constant and reached maximum adsorption at pH 7.5. The explanation could refer to the copper adsorption section. Meanwhile, for SCG, pH 4.5 was the optimum pH for Ni (II) removal. In contrast, the percentage removal of papaya seed powder remained almost constant in the range between 67 to 71%. This proved that pH did not have much influence on the Ni (II) adsorption on papaya seed powder binding sites.

In short, both Cu (II) and Ni (II) adsorption relied greatly on the solution pH. Cu (II) had higher affinity for adsorption on the three adsorbents at higher pH. Meanwhile, higher elimination of Ni (II) was attained at lower pH. The highest percentage removal of Cu (II) was at pH 9, while for Ni (II), adsorption was the best at pH 4.5.

#### 4.2.2 Effect of Initial Metal Concentration

Another critical parameter that influenced the removal efficiency was the initial metal concentration of solutions. Figure 4.9 presents the impact of initial Cu (II) metal concentrations from 4 to 12 mg/L on the removal efficiency of Cu (II) ions using SCG, papaya seed powder and eggshell powder.

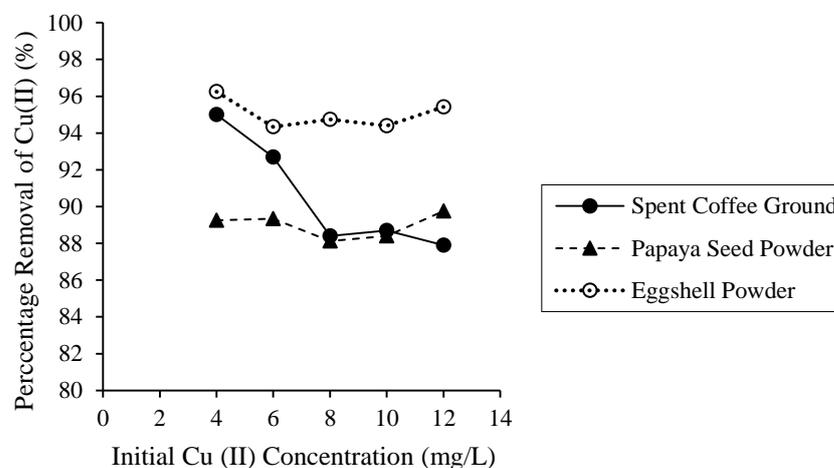


Figure 4.9: Effect of Initial Cu (II) Concentration on the Percentage Removal of Cu (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

Similar to the study of pH, eggshell powder exhibited the highest percentage removal of Cu (II) in general. Based on Figure 4.9, at low copper initial metal concentration, SCG and eggshell powder displayed the similar trend, where the percentage removal of Cu (II) decreased from 96.25% to 94.33% for eggshell powder and from 95% to 92.7% for SCG. Both adsorbents had achieved the highest percentage removal of Cu (II) at low initial metal concentration owing to the large surface area with specific binding sites available for adsorption to take place (Abdel-Ghani and El-Chaghaby, 2014). The adsorption performance of SCG was then followed by a sharp decline, and gradually decreased to 87.9% removal. As the initial metal concentration further increased, there was limited number of active adsorption sites available as the adsorption sites were entirely occupied (Shanthi and Selvarajan, 2013). This contributed to the situation that high number of Cu (II) ions were left un-adsorbed in the metal solution, and thus lower percentage removal was obtained (Naiya et al., 2009). For eggshell powder, at the range of 6 to

10 mg/L, the impact on the adsorption performance was not significant as the percentage removal revolved around 94%. Unlike previous studies by Naiya et al. (2009) and Shanthi and Selvarajan (2013), at 12 mg/L initial metal concentration, the adsorption increased to 95.42%. The papaya seeds powder exhibited much lower adsorption efficiency than other two adsorbents at low initial metal concentration, which was around 89%. This might be due to the difference in chemical structure and composition of the adsorbents. However, from 8 to 12 mg/L of initial metal concentration, the percentage removal of Cu (II) increased from 88.13% to 89.75%. To sum up, the adsorption of Cu (II) by SCG was influenced by the initial metal concentration. The decrease in Cu (II) adsorption as a result of higher initial metal concentration was evidently presented in Figure 4.9, whereas no specific trend was shown by papaya seed powder and eggshell powder.

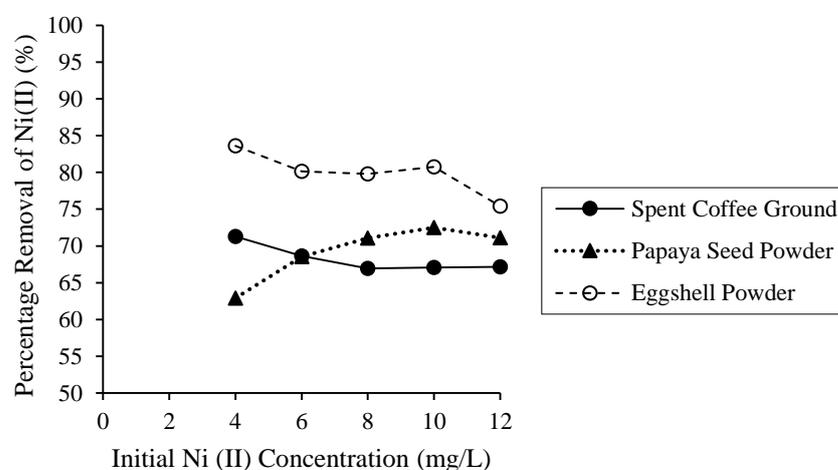


Figure 4.10: Effect of Initial Ni (II) Concentration on the Percentage Removal of Ni (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

Figure 4.10 illustrated the impact of initial Ni (II) metal concentration on adsorption using SCG, papaya seed powder and eggshell powder. The overall trend portrayed by eggshell powder was similar to Cu (II) adsorption by SCG. Maximum percentage removal of 83.61% was obtained at 4 mg/L initial metal concentration by eggshell powder due to its high availability of adsorption sites (Abdel-Ghani and El-Chaghaby, 2014). A further increase in initial nickel metal concentration resulted in lower percentage removal as the adsorption sites had been fully occupied (Shanthi and Selvarajan, 2013). Meanwhile, the percentage removal of Ni (II) using

SCG decreased from 71.29% to 66.92%. The adsorption reached its equilibrium at 66.92% as the percentage removal remained unchanged when initial metal concentration further increased. This might be explained by the same reason mentioned above, which there was no more binding site available for adsorption. However, for papaya seed powder, the percentage removal of Ni (II) rose from 62.91% until it reached maximum adsorption of 72.5% at 10 mg/L initial metal concentration. When the initial metal concentration exceeded 10 mg/L, a decline in percentage removal of Ni (II) was observed. In short, the overall trends of Ni (II) gave a clearer picture of the impact of initial metal concentration on adsorption.

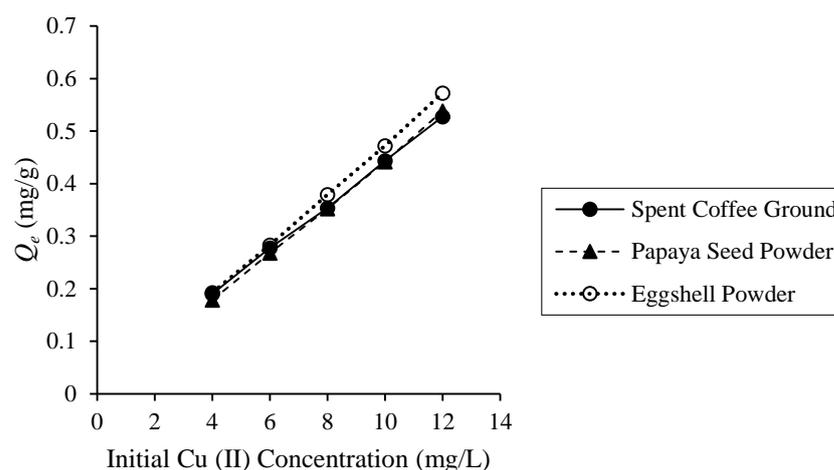


Figure 4.11: Effect of Initial Cu (II) Concentration on the Adsorption Capacity of Cu (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

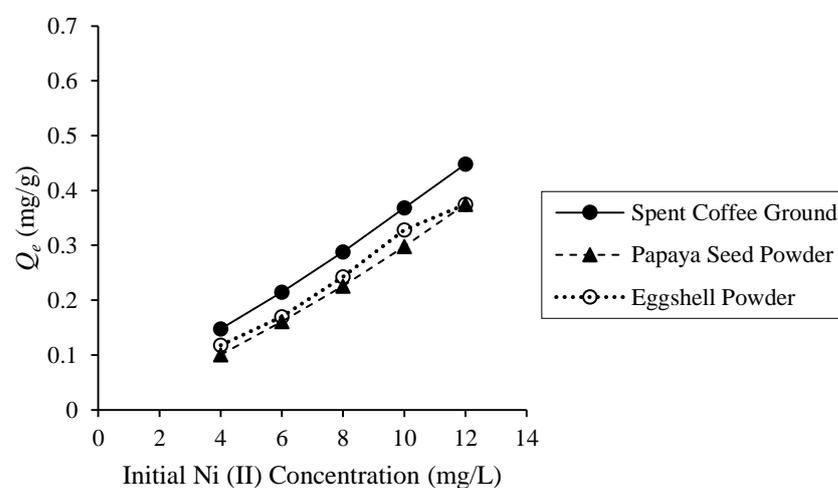


Figure 4.12: Effect of Initial Ni (II) Concentration on the Adsorption Capacity of Ni (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

Conversely, the adsorption capacity of adsorbents increased with initial metal concentration as shown in Figures 4.11 and 4.12. The initial metal concentration acted as the driving force to overcome the mass transfer resistance between the adsorbents and the adsorbates (Pahlavanzadeh et al., 2010). The trend of adsorption capacity could be explained with more interaction between the metal ions and the adsorbents at higher initial metal concentration (Rathinam et al., 2010). According to Chong, Chia and Ahmad (2013), the rise in adsorption capacity might be due to the decrease in quantity of metal ions adsorbed at higher initial metal concentration as there were insufficient adsorption sites. Driving force was created by high initial metal concentration to overcome the mass transfer resistances, which would restrict the adsorption of metal ions onto the adsorbent active sites (Abdel-Ghani and El-Chaghaby, 2014; Chong, Chia and Ahmad, 2013).

#### 4.2.3 Effect of Adsorbent Dosage

The adsorbent dosage could also be associated with the adsorption performance. Figure 4.13 demonstrated the effect of increasing adsorbent dosage from 2 to 10 g on the percentage removal of Cu (II) ions with SCG, papaya seed powder and eggshell powder.

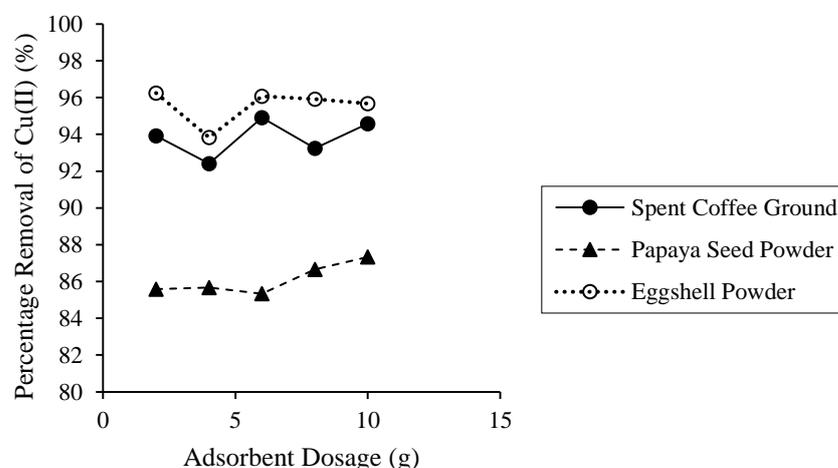


Figure 4.13: Effect of Adsorbent Dosage on the Percentage Removal of Cu (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

From Figure 4.13, it was portrayed that the Cu (II) ions adsorption decreased at first and then increased at the range of 2 to 6 g adsorbent dosage. The percentage removal of Cu (II) using SCG fluctuated between the range of 92% to 95%. Meanwhile, eggshell powder showed a reduction in adsorption efficiency when further increased the adsorbent dosage. The drop in then adsorption might be attributed to the precipitation or the chelation with different active binding sites on the adsorbent (Bamukyaye and Wanasolo, 2017). Eggshell powder achieved maximum adsorption efficiency of 96.25% at 2 g adsorbent dosage. Furthermore, Figure 4.13 also demonstrated that the adsorption efficiency of papaya seed powder remained marginal at first, then followed by a rise in adsorption when the adsorbent dosage further increased. This showed that adsorbent dosage of 6 g or lesser was not sufficient for adsorption of Cu (II). As the adsorbent dosage further increased, the percentage removal increased until the maximum adsorption efficiency of 87.33% was obtained. The same result was observed in the previous study of Kara and Demirbel (2012) as well as Govindarajan et al. (2011).

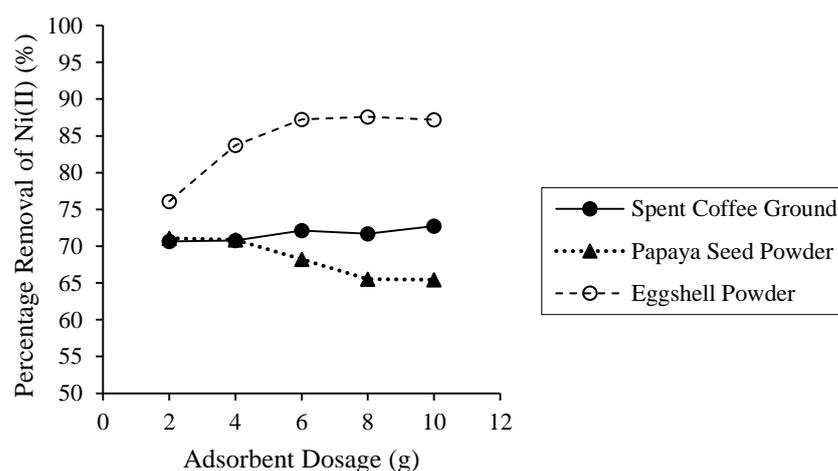


Figure 4.14: Effect of Adsorbent Dosage on the Percentage Removal of Ni (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

Figure 4.14 illustrated the effect of adsorbent dosage on the percentage removal of Ni (II) ions by SCG, papaya seed powder and eggshell powder. It was found that as the dosage of eggshell powder increased, the percentage removal of Ni (II) increased. Higher adsorbent dosage indicated higher surface area for adsorption and higher availability of binding sites for heavy metal ions (Belay and Hayelom,

2014). The limiting dosage for Ni (II) adsorption using eggshell powder was 6 g because the adsorption remained constant, even though higher amount of adsorbent dosage was added. This could be elucidated as the active binding sites on the surface of eggshell powder had been completely occupied with Cu (II) ions (Li et al., 2010). Hence, further increasing adsorbent dosage exhibited no significant influence on the adsorption as the equilibrium state of Ni (II) adsorption was reached (Li et al., 2010). The maximum adsorption of Ni (II) using eggshell powder was 87.6%.

On the other hand, SCG and papaya seed powder achieved around 71% of removal of Ni (II) using 2 g and 4 g of dosage. From Figure 4.14, inference was made that Ni (II) adsorption using SCG was almost independent of the adsorbent dosage due to the marginal difference of percentage removal of Ni (II) between 71% and 73%. For papaya seed powder, when the adsorbent dosage exceeded 4 g, the Ni (II) adsorption became lower. The decrease in adsorption performance could be correlated to the agglomeration of papaya seeds powder particles (Belay and Hayelom, 2014). This resulted in lower surface area exposed for adsorption owing to larger adsorbent particle size, resulting in lower percentage removal of Ni (II) ions. The maximum percentage removal of 71% was achieved with 2 g of papaya seeds powder.

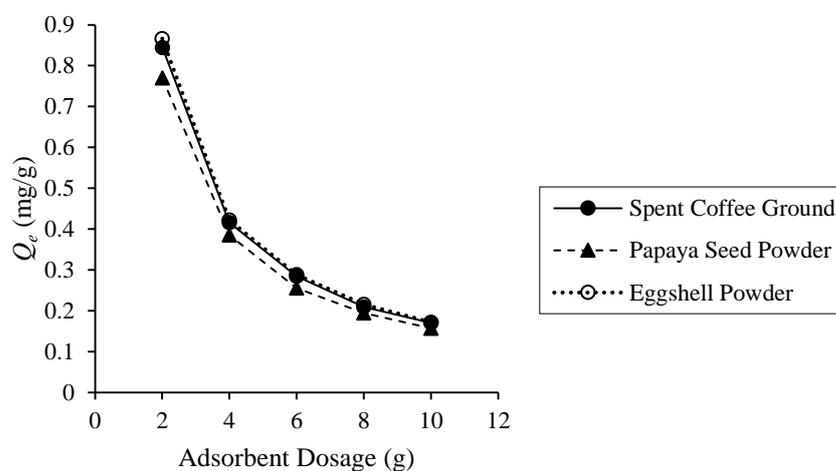


Figure 4.15: Effect of Adsorbent Dosage on the Adsorption Capacity of Cu (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

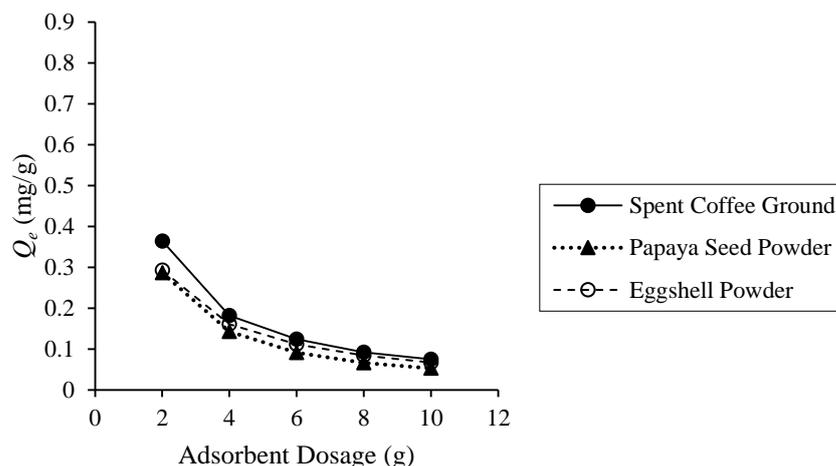


Figure 4.16: Effect of Adsorbent Dosage on the Percentage Removal of Ni (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

The overall trends of Figures 4.15 and 4.16 depicted that the adsorption capacity of adsorbents decreased as adsorbent dosage increased. As the adsorbent dosage increased from 2 to 10 g, the adsorption capacity of Cu (II) decreased from 0.87 to 0.17 mg/g, 0.84 to 0.17 mg/g and 0.77 to 0.16 mg/g, for eggshell powder, SCG and papaya seed powder respectively. During adsorption, some binding sites might not be saturated with Cu (II) ions as the increase in adsorbent dosage gave rise to high number of active binding sites (Yao, Qi and Wang, 2010; Eluke et al., 2017). In another study, Bamukyaye and Wanasolo (2017) claimed that the decline in adsorption capacity might be due to the aggregation, overcrowding and overlapping of the active binding sites of adsorbent. This resulted in high diffusion path length and low surface area available for adsorption (Eluke et al., 2017). Based on Figure 4.15, a sharp decline in adsorption capacity was observed when adsorbent dosage increased from 2 to 4 g. However, it was discovered that the adsorption capacity dropped gradually and steadily when the adsorbent dosage increased from 4 to 10 g. This showed that the aggregation impact was lower at higher adsorbent dosage as the decrease in adsorption capacity was decelerated (Eluke et al., 2017).

For Ni (II), the adsorption curve demonstrated the similar trend but lower adsorption capacity than Cu (II). As the adsorbent dosage increased from 2 to 10 g, the adsorption capacity of Ni (II) decreased from 0.36 to 0.07 mg/g, 0.29 to 0.07 mg/g and 0.29 to 0.05 mg/g, for eggshell powder, SCG and papaya seed powder

respectively. To summarise, the percentage removal and adsorption capacity of Cu (II) were generally higher than Ni (II).

#### 4.2.4 Effect of Contact Time

Effect of contact time was essential to identify the rapid and predominant adsorption stage and the optimum time required for eliminating heavy metal ions completely. Figures 4.17 and 4.18 showed the effect of 100 min contact time on the respective percentage removal of Cu (II) and Ni (II) ions with SCG, papaya seed powder and eggshell powder.

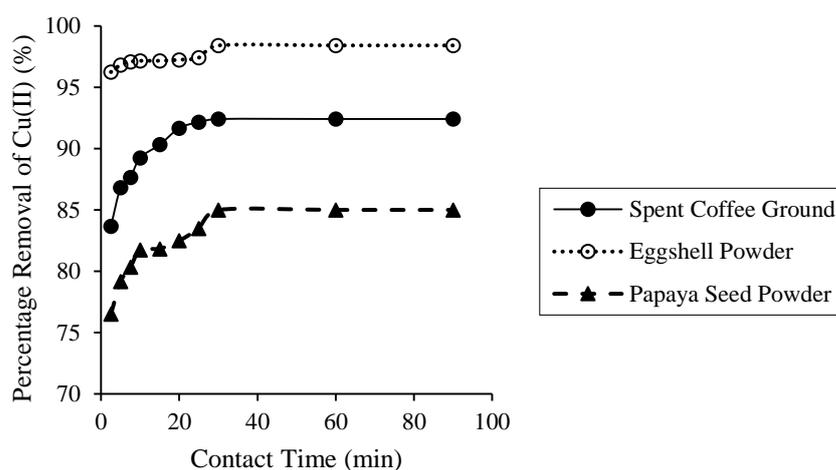


Figure 4.17: Effect of Contact Time on the Percentage Removal of Cu (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

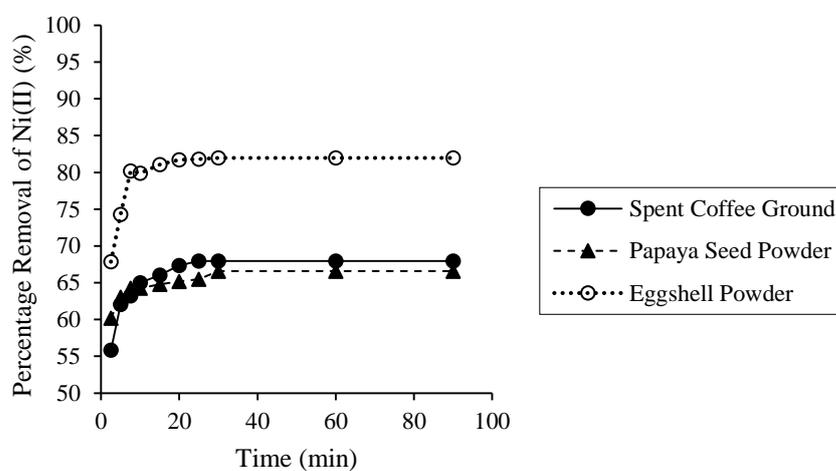


Figure 4.18: Effect of Contact Time on the Percentage Removal of Ni (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

Based on Figures 4.17 and 4.18, it was found that highest percentage removal of Cu (II) and Ni (II) ions was achieved by eggshell powder at 98.42% and 81.97%, followed by SCG at 92.42% and 67.94%, and the last was papaya seed powder at 85% and 66.58%, respectively. The overall adsorption on Cu (II) ions by three different adsorbents was higher than adsorption on Ni (II). Figures 4.17 and 4.18 could be split into three distinct stages. The first 10 min showed a rapid increase in percentage removal of metal ions, which was also named as instantaneous adsorption of ions stage (Wang and Wang, 2008). At this stage, the percentage removal could be seen to accelerate as external diffusion and surface adsorption take place due to more vacant active adsorption sites (Wang and Wang, 2008; Onundi et al., 2010). From 10<sup>th</sup> to 30<sup>th</sup> min, the rate of removal gradually decreased and began to approach equilibrium state. After 30<sup>th</sup> min, equilibrium state was attained as there was limited mass transfer of the metal ions from the metal solutions to the external adsorbent surface (Onundi et al., 2010). The percentage removal no longer increased after that. For Cu (II) adsorption, three adsorbents reached equilibrium state at the same time. However, for Ni (II) adsorption, eggshell powder reached equilibrium faster, followed by SCG and then papaya seed powder. This could be because of higher affinity of Ni (II) ions towards eggshell powder than the other two adsorbents (Onundi et al., 2010). To conclude, the optimum time needed for complete elimination of both metal ions was 30 min.

### 4.3 Selectivity Study

Selectivity was also another study which could affect the adsorption of metal ions. Figures 4.19-4.21 depicted the percentage removal of Cu (II) and Ni (II) from single copper and nickel solutions as well as Cu-Ni Binary-metals solution using SCG.

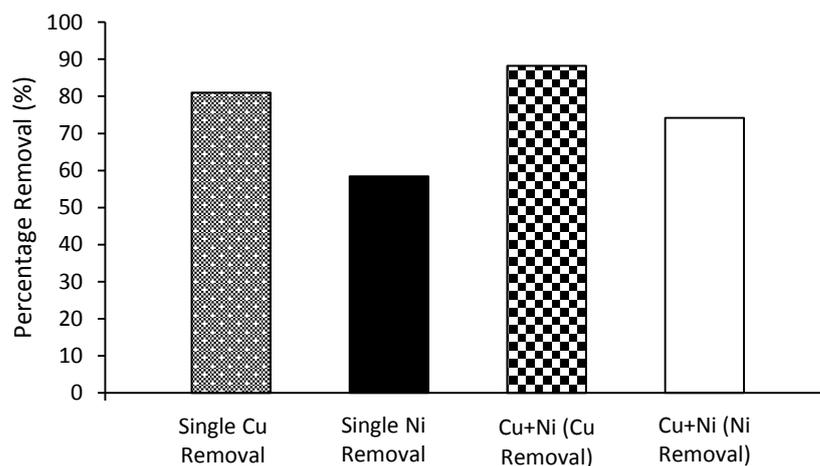


Figure 4.19: Comparison between Percentage Removal of Cu (II) and Ni (II) Metal Ions in Single Cu (II) and Ni (II) Solutions and Cu-Ni Binary-metals Solution by SCG

From Figure 4.19, it was clear that SCG exhibited higher selectivity towards Cu (II) than Ni (II) for adsorption in Cu-Ni binary-metals solution. This was because Cu (II) was more readily to form complex with ligand than Ni (II) ions (Koong et al., 2013). In addition, the difference in affinity of heavy metal ions towards the adsorption sites of the SCG could also explain why more Cu (II) was adsorbed (Davila-Guzman et al., 2016). Based on Figure 4.19, it could be concluded that Cu (II) had higher affinity towards the active sites of SCG than Ni (II). Moreover, Ni (II) was more unlikely to be adsorbed as displacement of Ni (II) by Cu (II) could happen at high solution concentration (Gao et al., 2009).

According to previous studies by Allen and Brown (1995), the presence of other metal ions would induce a competitive effect on the preferential removal of copper ions in multi-components solution. Another research by Al-Asheh and Duvnjak (1998) also highlighted the impact of metal co-ions on the removal of the major ions from a binary-metal solutions. The adsorbents were expected to be more efficient in single-component solution than in multi-components solution as there was no interference effect by other metal ions (Hadi, Barford, and McKay, 2013). However, Figure 4.19 demonstrated that higher percentage removal of Cu (II) and Ni (II) ions was achieved in Cu-Ni binary-metals solution than in their respective single-metal solution. This could be explained by the synergistic effect between Cu (II) and Ni (II) ions in the adsorption process (Hadi, Barford, and McKay, 2013). This result

was in agreement with previous study conducted by Triantafyllou, Christodoulou and Neou-syngouna (1999), which discovered an improvement in adsorption of Ni (II) ions in the presence of other metal co-ions.

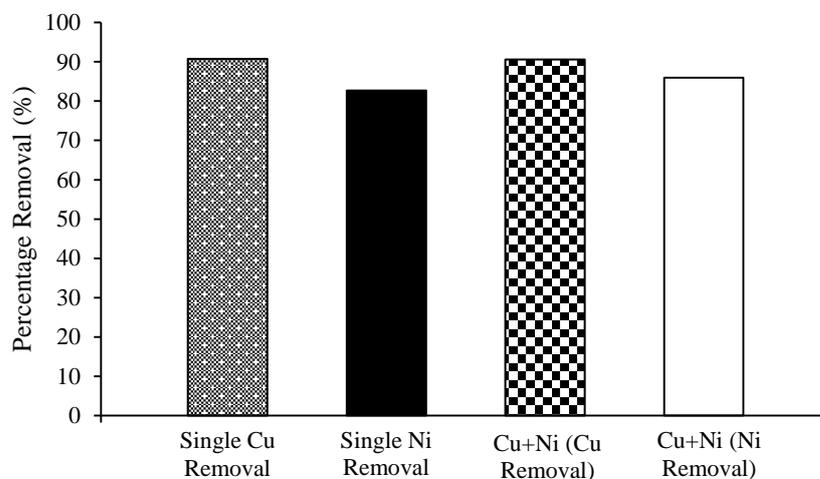


Figure 4.20: Comparison between Percentage Removal of Cu (II) and Ni (II) Metal Ions in Single Cu (II) and Ni (II) Solutions and Cu-Ni Binary-metals Solution by Papaya Seed Powder

Papaya seed powder had achieved around 90% percentage removal of Cu (II) for both single copper solution and Cu-Ni binary-metals solution. This could be explained by the presence of Ni (II) ions did not affect the removal of Cu (II) ions in binary-metals solution using papaya seed powder. Therefore, similar percentage removal was acquired for copper removal in single and binary-metals solutions. On contrary, for Ni (II) adsorption, the synergistic effect between Cu (II) and Ni (II) was once again proven to have enhanced the adsorption of Ni (II) as higher adsorption of Ni (II) was achieved in binary-metals solution than in single Ni (II) solution.

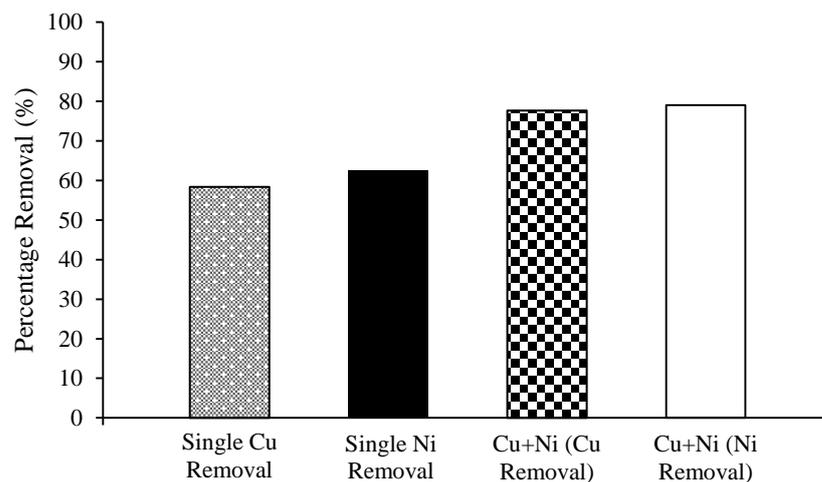


Figure 4.21: Comparison between Percentage Removal of Cu (II) and Ni (II) Metal Ions in Single Cu (II) and Ni (II) Solutions and Cu-Ni Binary-metals Solution by Eggshell Powder

A more significant difference between adsorption performances was displayed by eggshell powder. The percentage removal of metal ions was around 80% for adsorption in binary-metals solutions, whereas 60% percentage removal was for adsorption in single metal solutions. However, Ni (II) ions were adsorbed more than Cu (II) in both single and binary-metals solutions. This could be concluded that eggshell powder possessed more affinity towards Ni (II) adsorption.

#### 4.4 Isotherm Study

The data obtained from the contact time parameter was fitted into Langmuir and Freundlich isotherm models, respectively. Figures 4.22 and 4.23 presented the Langmuir isotherm plot for adsorption of Cu (II) and Ni (II) ions by SCG, papaya seed powder and eggshell powder. Table 4.2 summarised the findings from the Langmuir isotherm plots.

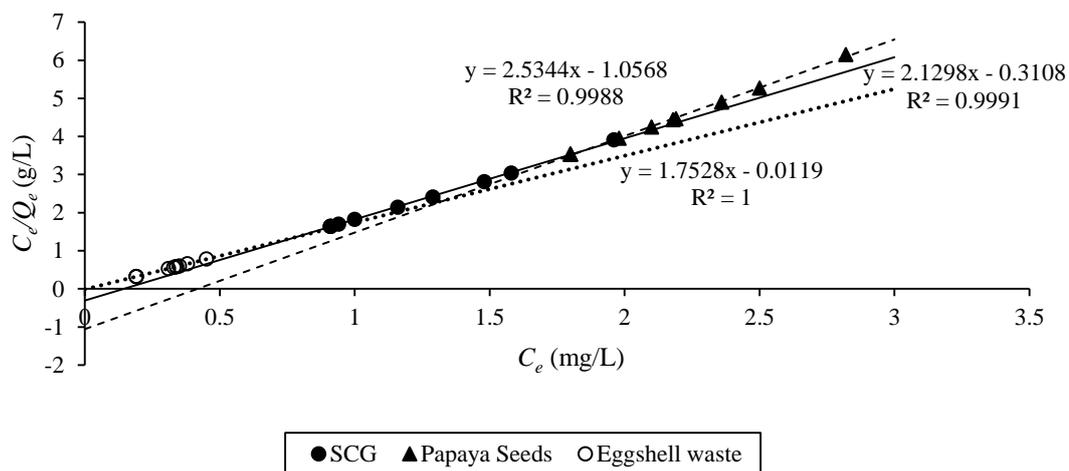


Figure 4.22: Langmuir Isotherm Plot for Adsorption of Cu (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

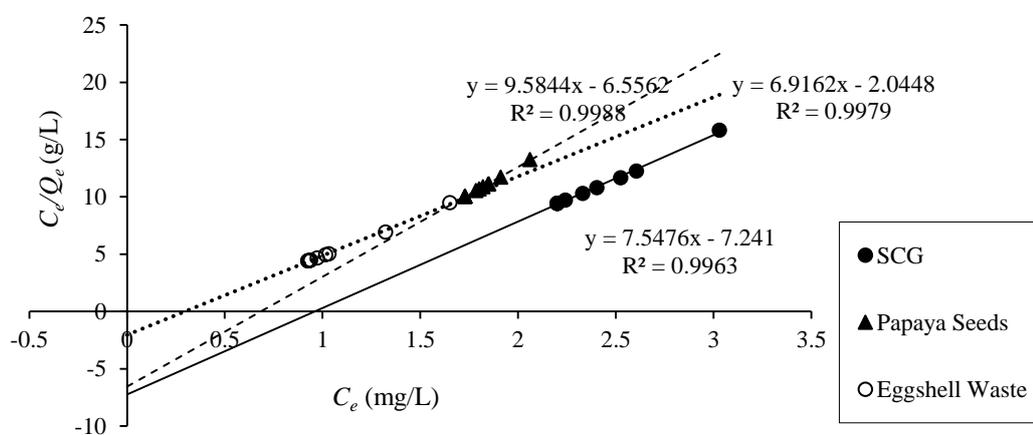


Figure 4.23: Langmuir Isotherm Plot for Adsorption of Ni (II) Ions by Different Types of Adsorbents

Table 4.2: R-squared and Constant Values of Langmuir Isotherm Model for Adsorption of Cu (II) and Ni (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

Types of Heavy Metal Ions	Cu (II)			Ni (II)		
	$R^2$	$Q_{max}$ (mg/g)	$K_L$	$R^2$	$Q_{max}$ (mg/g)	$K_L$
SCG	0.9991	0.4695	-6.8530	0.9963	0.1325	-1.0423
Eggshell Powder	1.0000	0.5705	-142.2982	0.9979	0.1446	-3.3821
Papaya Seed Powder	0.9988	0.3946	-0.9474	0.9988	0.1043	-1.4624

Based on Table 4.2, it was clearly shown that the R-squared values of Cu (II) adsorption were higher than those of Ni (II) adsorption for SCG and eggshell powder. The R-squared values obtained were close to 1, indicating that the data was well-fitted with Langmuir isotherm. For papaya seeds powder, the same R-squared values were obtained for Cu (II) and Ni (II) adsorption. The maximum adsorption capacities,  $Q_{max}$  of the adsorbents in Cu (II) adsorption were also higher than those in Ni (II) adsorption. According to Sing and Yu (1998), high adsorption energy,  $K_L$  resulted in high affinity of the adsorbents towards certain metals, and thus the R-squared values and  $Q_{max}$  increased.

The data was also fitted into the Freundlich isotherm model. Figures 4.24 and 4.25 depicted the Freundlich isotherm plot for adsorption of Cu (II) and Ni (II) ions by SCG, papaya seed powder and eggshell powder. Table 4.3 summarised the findings from the Langmuir isotherm plots.

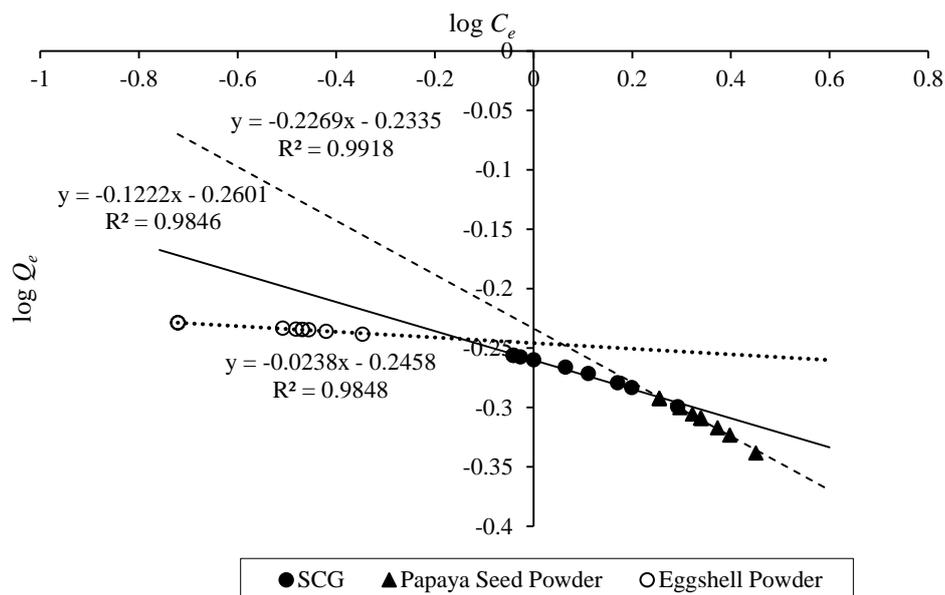


Figure 4.24: Freundlich Isotherm Plot for Adsorption of Cu (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

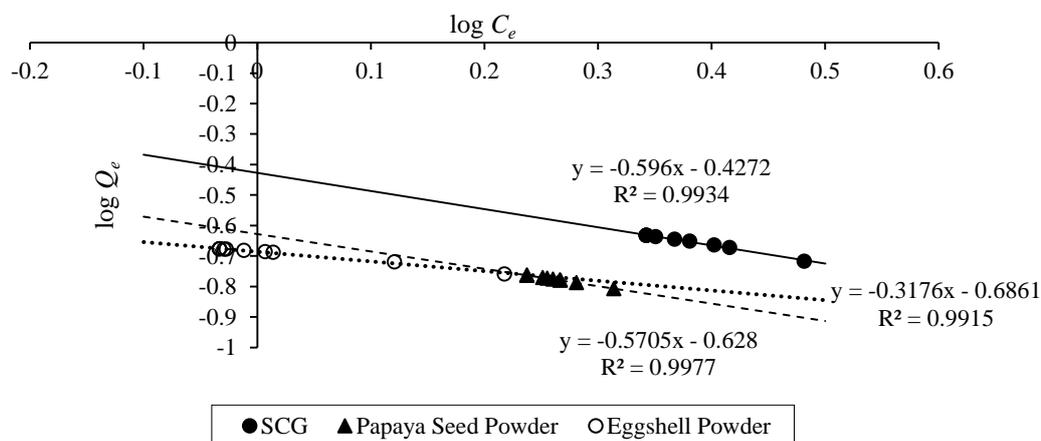


Figure 4.25: Freundlich Isotherm Plot for Adsorption of Ni (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

Table 4.3: R-squared and Constant Values of Freundlich Isotherm Model for Adsorption of Cu (II) and Ni (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

Type of Heavy Metal Ions	Cu (II)			Ni (II)		
	$R^2$	$1/n$	$K_F$	$R^2$	$1/n$	$K_F$
Types of Adsorbent						
SCG	0.9946	-0.1222	0.5841	0.9934	-0.5960	0.3739
Eggshell Powder	0.9848	-0.0238	0.5678	0.9977	-0.5705	0.2355
Papaya Seed Powder	0.9918	-0.2269	0.5494	0.9915	-0.3176	0.2060

The R-squared values of as high as 0.98 to 0.99 near to 1 presented by Freundlich isotherm also suggested that the data followed the isotherm well. By comparison, the data showed that the adsorption process followed Langmuir isotherm better than Freundlich isotherm as generally, the R-squared values proved the data had better correlation fit to the Langmuir isotherm. This could also mean that the adsorbents had homogeneous binding sites that were equally active with monolayer coverage (Hadi, Barford, and McKay, 2013). The binding of metal ions onto the adsorption sites of adsorbent surface was not affected by the neighbouring sites as the metal ions would not interact with each other (Hadi, Barford, and McKay, 2013). In short, the adsorption process of Cu (II) and Ni (II) following Langmuir isotherm was deemed as chemically equilibrated mechanism (Puranik, Chabukswar and Paknikar, 1995).

## 4.5 Kinetics Study

The kinetics data obtained from contact time parameter was fitted into adsorption kinetic models to observe and identify the rate limiting step of the adsorption process. Figures 4.26 and 4.27 depicted that the data of Cu (II) adsorption were fitted into pseudo-first-order and pseudo-second-model to observe the fitness of the graphs.

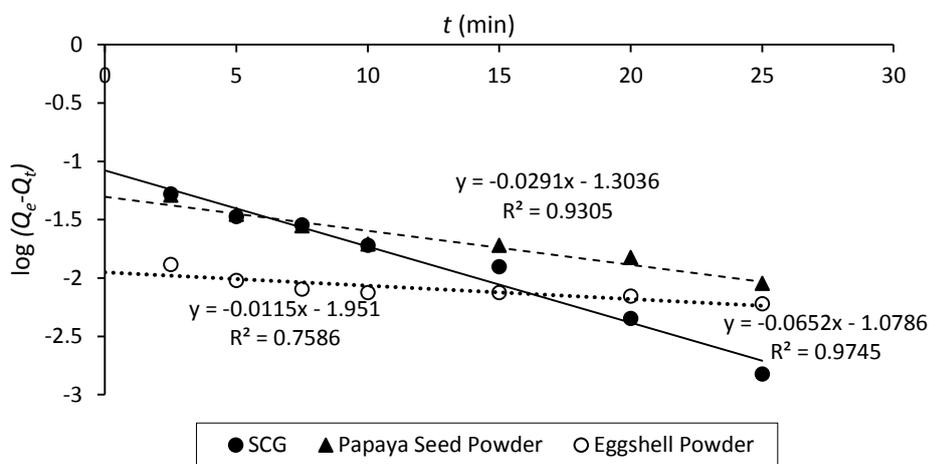


Figure 4.26: Pseudo First Order Plot for the Adsorption of 12 mg/L of Cu (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

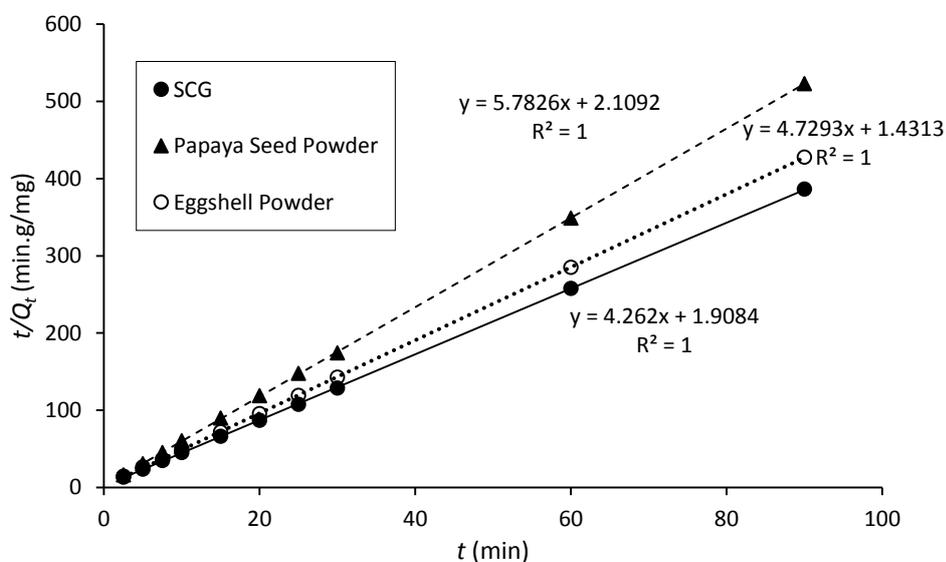


Figure 4.27: Pseudo Second Order Plot for the Adsorption of 6 mg/L of Cu (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

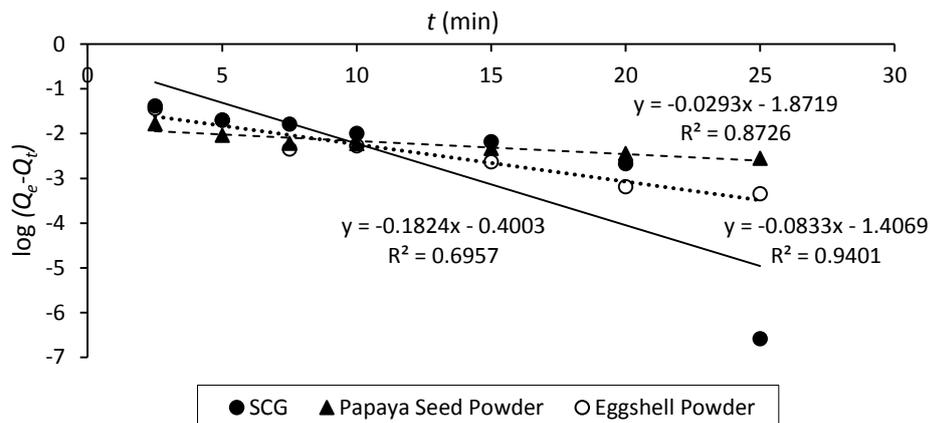


Figure 4.28: Pseudo First Order Plot for the Adsorption of 12 mg/L of Ni (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

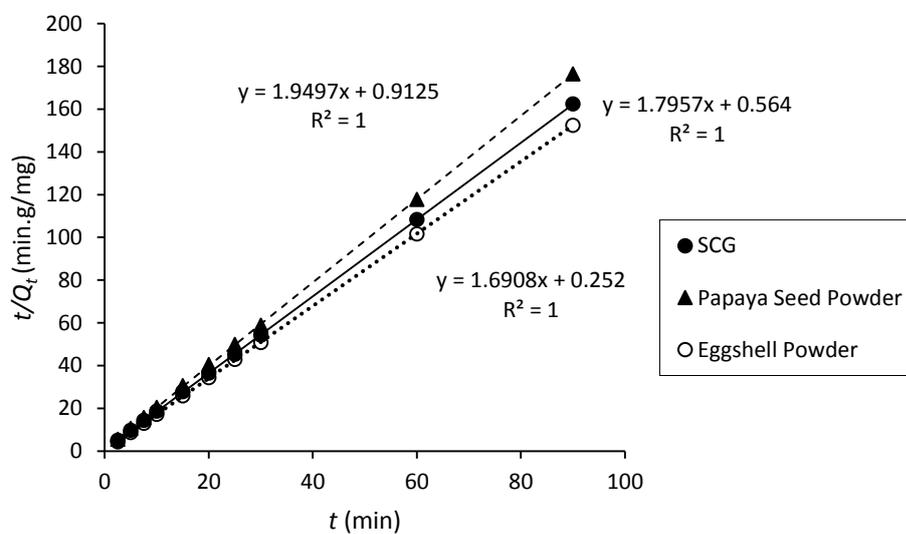


Figure 4.29: Pseudo Second Order Plot for the Adsorption of 6 mg/L of Ni (II) Ions by Different Types of Adsorbents

Table 4.4: R-squared and Constant Values of Pseudo-first-order and Pseudo-second-order Models for Adsorption of Cu (II) and Ni (II) Ions by SCG, Papaya Seed Powder and Eggshell Powder

Type of Heavy Metal Ions	Cu (II)		Ni (II)		Cu (II)		Ni (II)	
	Pseudo-first-order				Pseudo-second-order			
Type of Adsorbent	R <sup>2</sup>	<i>k<sub>1</sub></i>	R <sup>2</sup>	<i>k<sub>1</sub></i>	R <sup>2</sup>	<i>k<sub>2</sub></i>	R <sup>2</sup>	<i>k<sub>2</sub></i>
SCG	0.9745	-1.0786	0.6957	-0.4003	1	1.9084	1	0.5640
Eggshell Powder	0.7586	-1.9510	0.9401	-1.4069	1	1.4143	1	0.2520
Papaya Seed Powder	0.9305	-1.3036	0.8726	-1.8719	1	2.1092	1	0.9125

The adsorption process of Cu (II) and Ni (II) followed the pseudo-second-order model better than pseudo-first-order model. The R-squared values of pseudo-second-order plots for both adsorption processes were equivalent to 1, which proved the kinetic data were well-fitted to the pseudo-second-order model. This also indicated the adsorption processes were limited by the chemisorption which occurred at liquid-solid interface of the adsorbents (Tang et al., 2003). Meanwhile, relatively poorer linear correlations of coefficient of 0.7586 and 0.6957 displayed by eggshell powder and SCG, respectively proved that the adsorption processes of Cu (II) and Ni (II) did not follow pseudo-first-order model well.

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

To conclude, the potential of recycling SCG, papaya seeds and eggshell waste as adsorbents had been explored and they were found to be efficient in Cu (II) and Ni (II) ions removal from the synthetic wastewater. The morphology of SCG, eggshell waste and papaya seed had been characterised using SEM and FTIR. The cavities in SCG, macroporous structure and membrane fiber of eggshell waste as well as porous structure of papaya seed were observed. The FTIR spectrum demonstrated that amines, alkanes, alcohol and esters were present to enhance the adsorption of SCG. Amines and esters were found in papaya seed, while sulfate and 1,2-disubstituted or 1,2,3-trisubstituted were found in eggshell waste.

SCG, eggshell waste and papaya seed had been examined for their adsorption performance under different parameters studies, namely pH, initial metal concentration, adsorbent dosage and contact time. Eggshell waste was proven to be the best agro-waste adsorbents among three agro-wastes, followed by SCG and papaya seed.

The effect of pH study showed that SCG, eggshell waste and papaya seed presented different optimum adsorption performance at different pH. The highest percentage removals achieved by SCG, eggshell waste and papaya seed were 94.33% at pH 7.5, 97.83% at pH 9 and 98.33% at pH 3, respectively. It was also found that higher initial metal concentration resulted in lower percentage removal of metal ions. The optimum initial Cu and Ni concentration for adsorption by SCG and eggshell waste was 4 mg/L, whereas 10 mg/L of initial Ni concentration for papaya seed. An insignificant effect was observed on Cu (II) adsorption by papaya seed under the study of initial metal concentration. The adsorption capacities of SCG, eggshell waste and papaya seed increased linearly with the initial Cu (II) and Ni (II) concentrations.

Similarly, higher adsorbent dosage would result in lower percentage removal of metal ions. However, the adsorption capacities decreased with increasing adsorbent dosage. The optimum adsorbent dosage was 6 g for Cu (II) adsorption by

SCG and eggshell waste, and 10 g for papaya seed. Meanwhile, 2 g was sufficient for Ni (II) adsorption by papaya seed and 6 g was sufficient for eggshell waste. The results also showed that adsorbent dosage had no significant impact on Ni (II) adsorption by SCG. The optimum contact time required for the elimination of metal ions was 30 min and the predominant adsorption stage was found to be at the first 10<sup>th</sup> min.

Overall, SCG and eggshell waste exhibited better selectivity towards Cu (II) adsorption, whereas papaya seed showed more affinity towards Ni (II) ions. The adsorption process was well-fitted into the Langmuir isotherm, which assumed that monolayer sorption had occurred. The kinetics data followed the pseudo-second-order model with R-squared value equivalent to 1. This could be concluded that the adsorption process was limited by chemisorption.

## 5.2 Recommendations for Future Work

Through this research work, SCG, the potential for eggshell waste and papaya seed to be reused as low-cost adsorbents in heavy metal removal have been proven. Hence, extended studies on these adsorbents in heavy metal removal can be conducted. There are several recommendations to be made in order to improve existing experimental results as well as to provide better insight and scope for other researchers in future research:

- More parameter studies such as effect of particle sizes, agitation speed and so forth can be conducted to better understand the adsorption performance using these adsorbents.
- The adsorption study in continuous mode can be conducted to simulate the adsorption in industrial wastewater.
- Chemical modifications of these adsorbents can be performed in order to increase the number of functional groups that are useful for the adsorption of Cu (II) and Ni (II) (Vieira and Volesky, 2000).
- Surface modifications by physical pre-treatment can be conducted to alter the ability of adsorbency and ion exchange (Gupta, Nayak and Agarwal, 2015).
- Characterisation of pore size distribution of SCG, eggshell powder and papaya seed powder could be performed for more in-depth study of adsorption related to the surface area of adsorbents.

- Application of SCG, eggshell powder and papaya seed powder as adsorbents in other heavy metal removal can be further explored.
- The adsorption using industrial electroplating wastewater can be carried out to analyse the feasibility of these adsorbents in actual heavy metal removal.

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