REMOVAL OF CADMIUM FROM WATER USING BIOSORPTION PROCESS

DAI XIAO JIA

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
Universiti Tunku Abdul Rahman

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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.

Signature :

Name : DAI XIAO JIA

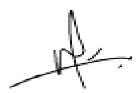
ID No. : 1602798

Date : 4/5/2021

APPROVAL FOR SUBMISSION

I certify that this project report entitled **"REMOVAL OF CADMIUM FROM WATER USING BIOSORPTION PROCESS"** was prepared by **DAI XIAO JIA** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature : 

Supervisor : Dr. Ng Yee Sern

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ABSTRACT

Human activities such as mining, industrialization and agricultural activities largely contribute to the release of divalent heavy metals such as cadmium had led to contamination of water sources. Cadmium contamination in water will directly threaten the human health. Therefore, the established threshold concentration of cadmium in raw water by World Health Organization (WHO) is 0.003 mg/L only. The technical feasibility of biosorption process which utilizing low-cost biosorbents in removing cadmium from water was evaluated in this project. Overall, the literature review in this project was conducted by narrative review approach. The relevant information on the biosorbents that had been used in the removal of cadmium from water was obtained through different online sources and the literatures were screened according to the pre-set criteria: 1) literatures published on past 12 years, 2) important keywords are included, 3) published in English language, 4) proper citation and references. After that, the relevant experimental data were extracted from the literatures and gathered using Excel database and dialogical narrative analysis was implemented in presenting the findings for this research work. Among different types of biosorbents, agricultural wastes were found to be the most efficient biosorbent for cadmium removal. From the effect of parameters study, it was discovered that the maximum cadmium uptake was normally obtained at slightly acidic to neutral solution pH, high solution to biosorbent dosage ratio and optimum contact time of within three hours. The responsible functional groups in cadmium biosorption are acidic, amino, hydroxyl and carboxyl groups. The biosorption of cadmium are reported to follow Langmuir isotherms and pseudo-second order kinetic models. From the results analysis, it is predicted that avocado peel has potential to be a promising biosorbent in removing cadmium from water where the biosorption process is predicted to happen at a condition of pH = 4−7, solution to biosorbent dosage ratio ≤1000 mL/g and contact time within three hours. In conclusion, biosorption process is efficient in removing cadmium from water as it is environmentally friendly and cost effective.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS / ABBREVIATIONS

C_e	solute concentration at equilibrium, mg/L
C_i	initial concentration of cadmium standard solution, mg/L
K_L	Langmuir equilibrium constant of adsorption capacity, L/mg
k_F	Freundlich constant of adsorption capacity
k_1	first order rate constant, min^{-1}
k_2	second order rate constant, $\frac{g}{mg \cdot min}$
m	mass of biosorbent, g
n_F	Freundlich constant of adsorption intensity
q_e	biosorption capacity per unit mass of biosorbent at equilibrium, mg/g
q_{max}	maximum theoretical biosorption capacity, mg/g
q_t	biosorption capacity per unit mass of biosorbent at time (t), mg/g
t	time, min
V	volume of cadmium stock solution, L

BET	Brunauer-Emmett-Teller
CAGR	Compound Annual Growth Rate
CEMACS	Centre for Marine and Coastal Studies
DoE	Department of Environment
EDX	Energy Dispersive X-ray
EQA	Environmental Act Quality
FTIR	Fourier Transform Infrared Spectroscopy
$KMnO_4$	Potassium Permanganate
SEM	Scanning Electron Microscopy
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Water makes up 70% of our mother Earth and it is an essential part in our daily life as drinking water. All the flora and fauna that survive on Earth requires water to sustain their life. Therefore, water plays an important role for all living things. Water is very precious although it is considered as renewable sources, as water pollution has recently become one of the most worrying affairs in the world. Water pollution is the water that is being contaminated and harmful to human health and ecological system. Water can be polluted by direct or indirect sources.

The pollutants in water consist of different chemicals and pathogens which have certain undesirable effects to the ecosystem. Therefore, it is significant to extract those pollutants from water system especially the divalent heavy metals. Divalent heavy metal such as cadmium (II) ion is toxic and carcinogenic. It is usually being released into the environment in liquid effluent by fertilizers, natural deposits erosion, metal refineries and corrosion of galvanized pipes. The exposure to cadmium ion for a long term is very harmful to human being as it is a potential carcinogen (Bloomfield, 2017). Therefore, the removal of cadmium ion from raw water is utmost important. The threshold concentration of cadmium ion in raw water is 0.003 mg/L (World Health Organization, 2011).

There are a lot of conventional methods that could be implemented in order to extract the heavy metal ions from water. Common conventional methods in water treatment include reverse osmosis, chemical precipitation, electrochemical treatment, membrane filtration as well as ion exchange are normally cost intensive, as they involve the use of chemicals and specific equipment. Adsorption is a technology that is widely applicable in wastewater treatment. However, the activated carbon used in this technology is normally costly.

In contrast, biosorption is an alternative method which can be applied to extract the heavy metals from water. Biosorption is a process that employs biological materials to accumulate the heavy metals. Biological compounds include bacteria, fungi, algae and agricultural waste can be employed to extract the heavy metal ions from water. These compounds used to carry out biosorption in heavy metal ions removal are abundantly available and are able to obtain easily. Therefore, biosorption is a greener process that has low operation cost, creates relatively less wastes or sludges and is easy to operate.

There are a lot of research have been conducted regarding the use of different biosorbents such as bacteria, fungi, algae and agricultural waste in the removal of cadmium ion. Therefore, this study attempts to evaluate biosorption performance by different biosorbents and the effect of operating parameters on the cadmium biosorption as well as to analyse the technical feasibility of avocado peel to remove the cadmium ion from water based on the reported literature.

1.2 Importance of the Study

Water bodies tend to be contaminated by different pollutants especially heavy metals. Therefore, in order to have safe potable water, water treatment is often needed to extract the heavy metals and organic compounds. However, the conventional water treatment methods that are commonly used are costly and may generate undesirable sludges. In contrast, biosorption is an alternative method to treat the contaminated water. This process could be carried out by utilising the biosorbent, which is normally low cost and easily available. There are various types of biosorbent can be used especially fruit waste. Therefore, it is important to determine the feasibility of biosorbent in removal of cationic contaminant, cadmium ion in this study. If the biosorbent is feasible to remove the cationic contaminant, it is both economical viable and green to be implemented in future.

1.3 Problem Statement

As reviewed in Section 1.1, water pollution has been the major concern of public nowadays. Water pollution is an unavoidable consequence which is mainly arises of human activities such as mining, industrialization and agricultural activities. These human activities contribute to the release of waste especially the heavy metals and contaminate the water sources.

The heavy metal pollutants will destroy the healthy ecosystem. These cationic contaminants, especially cadmium ion is hazardous to human as it is carcinogenic. Therefore, potable water always needs to be treated before distributing as drinking water supply, so that the heavy metal concentration can be kept at an acceptable level and thus is safe for drinking purpose. Due to the high capital cost of conventional wastewater technologies and expensive activated carbon as adsorbent, the low-cost biosorbent is proposed to be alternatively used to remove the heavy metal present in water. Therefore, the investigation and evaluation of ability of biosorbents in the removal of cadmium from water is necessary to be conducted.

1.4 Aim and Objectives

The principal objective of this project is to investigate the technical feasibility of using biosorbent to remove the cationic contaminant, cadmium ions (Cd^{2+}) from water. There are also several objectives as listed below should be accomplished upon the end of this project.

(i) To evaluate the use of different types of biosorbents in the removal of cadmium from water.
(ii) To examine the effects of operating conditions on the removal of cadmium from water using biosorption process.
(iii) To identify the removal mechanisms for the biosorption of cadmium from water.
(iv) To evaluate the suitability of avocado peels as biosorbent in the removal of cadmium from water.

1.5 Scope and Limitation of the Study

In this study, biosorption process is utilized to remove the selected cationic contaminants which is cadmium from water. Few scopes are proposed to achieve the expected broad outcomes of this study.

(i) Evaluation on types of biosorbent used for cadmium removal from water are based on past 12 years of publications.
(ii) Investigation of the effect of operating parameters on adsorption uptake of cadmium such as pH, solution to biosorbent dosage ratio, and contact time.

(iii) Identification of the main mechanisms involved in the cadmium biosorption from water and study on the functional groups that are responsible in providing better biosorption.

(iv) Evaluation on the suitability of avocado peels as biosorbent in cadmium removal are based on the process, biomass and effluent characteristics as well as the functional groups available.

The major limitation of this study would be the prohibition to conduct the laboratory work on account of coronavirus pandemic. There is no experimental investigation could be conducted to determine the feasibility of avocado peel as biosorbent to remove cadmium from water. Therefore, the cadmium uptake rate and the biosorption capacity of avocado peel as biosorbent cannot be evaluated experimentally. Instead, the feasibility of avocado peel is predicted based on the analysis of published literature.

1.6 Report Outline

A brief overview and background of this project are discussed in Chapter 1 together with the problem statement as well as the importance of the study. Besides, the main objective and several expected outcomes of this study are also listed in Chapter 1. The detailed literature review of the related research or journals on biosorbents, cationic contaminants and common conventional water treatment technologies and experiments regarding biosorption are explained in Chapter 2. Prior empirical study of the parameter effects on biosorption capacity, kinetic studies of biosorption and modelling of biosorption isotherms are conducted under this chapter. Chapter 3 manifests about the framework methodology for the literature review study on different types of biosorbent, effects of operating condition on biosorption efficiency and removal mechanisms in removing the cationic contaminants from water. The results obtained by conducting the literature review are then discussed, elaborated and interpreted in Chapter 4. Lastly, Chapter 5 will conclude the research study of this project with some recommendations and improvements.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Heavy Metal Pollution

Heavy metals by definition are the metal in which the density is high and is toxic at low concentration (Lenntech, 2020). Heavy metals are the most commonly found metallic element which can either exist naturally or arise from human activities. Heavy metal pollution has been the main concern of the public nowadays. This is because heavy metals have significant effect to environment and hazardous to human health even at low concentrations (Beni and Esmaeili, 2019). It exists persistently in the environment and cannot be degraded or destroyed (Duruibe, Ogwuegbu and Egwurugwu, 2007).

Heavy metal contaminants usually can be found in soil, air and water. Heavy metal can produce undesirable side effects in both short term or long-term exposure. Water is the most common sources that has been polluted by heavy metal. In recent years, there are many news regarding heavy metal pollution in water being reported globally. Due to the global industrialization activities and improper ways of waste disposal, heavy metal pollution becomes one of the biggest issues. The global industrialization activities are anthropogenically such as mining, metal refineries, construction work, coal burning and industrial production process (Lixandru, 2017).

The main source of heavy metal pollution is the waste generated from industrial plant. The waste effluent containing heavy metal discharge from the factories to the nearby water sources such as river will contaminate the water directly. Water contaminated by high concentration of toxic heavy metal if not well-treated, may threaten the aquatic life as well as human health if it is being used as the potable water resources.

To minimize the heavy metal pollution in water, Department of Environment (DoE) Malaysia has established Environmental Quality (Industrial Effluent) Regulations 2009. There are two effluent discharge standards set by Environmental Act Quality (EQA) 1974. Standard A is for raw water intake discharge upstream, whereas, Standard B is for raw water intake discharge downstream. Table 2.1 shows the acceptable limit of heavy metals in industrial effluent discharge as listed in the fifth schedule of the regulation according to Department of Environment Malaysia, 2009.

Table 2.1: Acceptable limit of Heavy Metals in Industrial Effluent Discharge of Standard A and B.

Heavy Metals	**Threshold Concentration (mg/L)**	
	Standard A	**Standard B**
Aluminium	10.0	15.0
Arsenic	0.05	0.10
Barium	1.0	2.0
Boron	1.0	4.0
Cadmium	0.01	0.02
Chromium, Hexavalent	0.05	0.05
Chromium, Trivalent	0.20	1.0
Copper	0.20	1.0
Cyanide	0.05	0.10
Iron (Fe)	1.0	5.0
Lead	0.10	0.50
Manganese	0.20	1.0
Mercury	0.005	0.05
Nickel	0.20	1.0
Selenium	0.02	0.50
Silver	0.10	1.0
Tin	0.20	1.0
Zinc	2.0	2.0

2.2 Cationic Contaminants

Cationic contaminants are normally the divalent heavy metals which is positively charged. Divalent heavy metals that are commonly found in wastewater including arsenic, copper, cadmium, lead, mercury, nickel and zinc. These cationic contaminants are hazardous and may cause severe health hazards if the concentration in potable water exceeds the permissible limit established by World Health Organization (WHO) or Ministry of Health Malaysia. Therefore, it is important to identify the acceptable value of metal content in raw water to ensure the drinking water quality. In Malaysia, the water pollution in heavy industrial and large population area are most commonly caused by copper, zinc and lead ion (Shazili, et al., 2006). Recently, cadmium, lead and nickel ion has also become the hot issue in causing water pollution in Penang National Park (Kaur, 2019). The threshold concentration established by World Health Organization (2011) of several common cationic contaminants which are found in the wastewater of Malaysia are tabulated in Table 2.2. There is no health concern at levels found in drinking water for zinc ion, hence there is no any guideline limit established by WHO, but there is an acceptable limit being set according to Ministry of Health Malaysia (2016).

Table 2.2: Threshold Concentration of Several Cationic Contaminants.

Cationic Contaminants	Threshold Concentration (mg/L)
Cadmium (Cd^{2+})	0.003
Copper (Cu^{2+})	2.0
Lead (Pb^{2+})	0.01
Nickel (Ni^{2+})	0.07
Zinc (Zn^{2+})	3.0

Zinc and copper ions exist naturally in water, air and soil. Both of them are considered as essential trace elements in our daily life as long as they do not exceed the allowable threshold concentration. Zinc can be found easily in foodstuffs and drinking water in the form of salt or organic compounds (World Health Organization, 2011). If the zinc concentration in drinking water is too high, it may also cause severe health effect such as nausea, vomiting, anaemia and cholesterol problems (Gautam, et al., 2014). Besides, high copper concentration in potable water may cause health issues due to short-term or long-term exposure. Copper concentrations in potable water vary widely, with the corrosion of interior copper plumbing as the primary source (World Health Organization, 2011). Exposure to high copper concentration in short period of time will cause eyes, nose and oral irritations, diarrhea and nausea, whereas, lifetime exposure will result in kidney damage or death (Gautam, et al., 2014).

Moreover, contribution of lead ion is mainly coming from the lead-acid batteries, solder and alloys production (World Health Organization, 2011). High concentration of lead in potable water may cause serious health hazards in kidney, nervous and reproductive system. On the other hand, according to Gautam, et al. (2014), nickel ion is used in manufacturing of automobile and aircraft parts, electroplating, batteries, coins, paint formulation and cigarettes smoking. Higher uptake of nickel ion will lead to cancer development, heart disorder, allergic reactions, respiratory failure and birth defects (Lenntech, 2020). Next, cadmium, which is the investigated cationic contaminant in this study, its properties, applications, sources of contamination, contamination level, health hazards and environmental impact are further discussed in Section 2.3.

2.3 Cadmium

In 1817, Prof. Freidrich Stromeyer, a German chemist discovered cadmium. It is found to be chemically similar to zinc and mercury (Connor, 2020). Cadmium is a transition metal in Period 5 with an atomic mass of 112.411 g/mol as well as atomic number of 48 and density of 8.65 g/cm^3 at 20°C. It exists as soft and bluish white solid metal at room temperature. The boiling point and melting point of cadmium are at 767°C and 321°C respectively. Cadmium has a thermal conductivity of 97 W/m·K and 2300 J/kg·K specific heat capacity. The oxidation state of cadmium is positive two and has electronegativity of 1.69. It has a hexagonal close-packed crystal structure and is a ductile and very malleable metal. According to Lenntech (2020), cadmium is acid-soluble but insoluble in alkali.

The applications of cadmium in industries is very wide especially in batteries and alloys production. Cadmium is commonly applied in nickel-cadmium acid batteries. Besides, the electroplating coatings industry also implement cadmium as anticorrosive agent to galvanize steel. Furthermore, cadmium is used as plastic stabilizer and colour pigments. Due to the strong neutron absorption ability, cadmium is also being utilized as barrier for nuclear fission control in nuclear industry (Lenntech, 2020).

2.3.1 Health Hazards of Cadmium

Cadmium is normally uptaken by human through food sources. The ingestion of high concentration of cadmium is critical to human health. Health effects may arise in consequence of short-term and long-term exposure of cadmium. Short-term exposure to high concentration of cadmium will cause nausea, vomiting, stomach-ache, diarrhea, muscle cramp and sensory disturbances. On the other hand, long-term exposure to cadmium that exceeds the threshold concentration will damage liver, bone, blood and kidney (Water Quality Association, 2013).

Cadmium being uptaken by human will be first transported to liver through blood circulation system and then binds with proteins and forms complexes and eventually being transported to the kidneys. According to World Health Organization (2011), the main target organ for cadmium toxicity is the kidneys. Accumulation of cadmium primarily takes place in the kidneys and has 10 to 35 years biological half-life in humans. This is also supported by United States Environmental Protection Agency (2020) which states that kidney damage is the potential health hazards as a result of long-term exposure of cadmium. The cadmium poisoning will lead to “Itai-Itai” disease, which is discovered in Japan (Volesky, 1990). Apart from that, prolonged exposure to cadmium through ingestion and inhalation also has the potential to cause development of cancer (Kubier, Wilkin and Pichler, 2019).

2.3.2 Environmental Impact of Cadmium

The discharge of effluent which contains cadmium from the industries or household may eventually end up in soils or sediments. High concentration of cadmium in water and soil will threaten the soil and aquatic ecosystem. The cadmium in the water will leach into soil and strongly adsorb to the organic matter in the soil. This condition is very dangerous as the acidified soil will enhance the uptake of cadmium by plants. The animals which acquire plants as their food source may also consume the cadmium directly and the cadmium accumulation in their body will cause kidney damage. Other than that, this leaching of cadmium into the soil will also affect the soil processes of microbes and poison the organisms living in the soil.

Other than polluting the soil, the cadmium that is released to the water can bioaccumulate in the aquatic organisms such as fishes, prawns and crabs via ingestion. Different aquatic organisms may have different susceptibility to cadmium. For instance, freshwater organisms are less resistant to cadmium poisoning than saltwater organisms. Besides, animals that are eating or drinking the sources which are being contaminated by cadmium will possibly suffer from liver disease, high blood pressure and neurological disorder (Lenntech, 2020).

2.3.3 Contamination of Cadmium

The contamination of cadmium comes from a few sources. First, cadmium can be discovered naturally in the Earth's crust as it always exists together with zinc, as well as in lead and copper ores. The erosion of these natural deposit will release cadmium into water. Next, during smelting of zinc from zinc ore, cadmium will be generated as a by-product (Lenntech, 2020). Besides, cadmium can also be released to environment through various human activities include tobacco smoking, burning of fossil fuel and municipal waste (Bloomfield, 2017). Cadmium is mostly found in drinking water supply due to the corrosion of galvanized plumbing, industrial waste contamination, and contamination of surface water by fertilizers. The zinc impurities of the galvanized pipes, solders as well as metal fittings may also cause cadmium contamination in potable water as reported by World Health Organization (2011). Moreover, the discharge of effluent from metal refineries and waste runoff from paints as well as batteries also contribute to cadmium contamination in drinking water (United States Environmental Protection Agency, 2020).

Several journals have reported that water has been polluted by cadmium in these few years. Table 2.3 shows the contamination level of cadmium in different water sources at different locations of several countries in the past decades. It can be summarized that cadmium contamination level in different wastewater sources are ranged from 0.390 mg/L to 33.9 mg/L and groundwater is polluted by cadmium with a range of 0.040 mg/L to 0.580 mg/L. The contamination level of cadmium was reported to be 32% higher than usual in Teluk Bahang coastal waters by Universiti Sains Malaysia’s Centre for Marine and Coastal Studies (CEMACS) as stated by Kaur (2019). According to Raman (2019), the coastal water is polluted by cadmium with a concentration of 0.065 mg/L. The acceptable limit of cadmium concentration in drinking water is only 0.003 mg/L as shown in Table 2.2. However, according to Table 2.3, the cadmium contamination level is exceeding the threshold concentration. Therefore, the cadmium contamination in water has become an issue and needs to be overcomed to reduce the health and environmental impacts.

Table 2.3: Cadmium Contamination Level in Water.

Country	Categories of Water	Location	Cadmium Contamination Level (mg/L)	References
Malaysia	Wastewater from Industrial Effluent	Recycled paper mill wastewater, Penang	0.390	Hassan, et al., 2014.
India		Engineering industry wastewater, Taloja Industrial Estate, Mumbai	24.4-26.0	Lokhande, Singare and Pimple, 2011.
		Paper mill industry wastewater, Taloja Industrial Estate, Mumbai	20.0-27.5	
		Fine chemicals industry wastewater, Taloja Industrial Estate, Mumbai	28.8-33.9	
		Dyes industry wastewater, Taloja Industrial Estate, Mumbai	16.7-29.9	
		Electroplating industry wastewater, Tamil Nadu	1.982	Rani, et al., 2010.
Saudi Arabia		Riyadh City industrial wastewater	8.940	Al-Jlil, 2010.

Table 2.3: Continued.

Country	Categories of Water	Location	Cadmium Contamination Level (mg/L)	References
Malaysia	Coastal Water	Teluk Bahang coastal water, Penang	0.065	Raman, 2019.
India	Groundwater	Shahjehanpur groundwater	0.060	Idrees, et al., 2018.
		Bareilly groundwater	0.070	
		Moradabad groundwater	0.060	
		Rampur groundwater	0.050	
		Krishna Vihar groundwater	0.280	Kubier, Wilkin and Pichler, 2019
		Cauvery River basin groundwater	0.060	
		Haridwar groundwater	0.040	
		Unnao groundwater	0.074	
China		Xiangjiang River groundwater	0.474	
Nigeria		Ikare groundwater	0.580	

2.4 Common Water Treatment Technologies

Heavy metals removal from water can be done through varying reliable techniques. Conventional water treatment technologies that are well established and implemented include reverse osmosis, chemical precipitation, electrochemical treatment, membrane filtration as well as ion exchange. The working principles, applications, benefits and limitations of these technologies are further discussed in Sections 2.4.1–2.4.5.

2.4.1 Reverse Osmosis

Heavy metals removal through reverse osmosis is a process that removes the metal ions from the solution by utilizing the semipermeable membrane and it is driven by pressure (Malaed and Ayoub, 2010). An applied pressure which is greater than the osmotic pressure of the solution is required so that the solution can flow through and prevent the backflow of the solution. The semipermeable membrane enables the water to flow through against the concentration gradient. However, the movement of heavy metals is restricted from semipermeable membrane. Therefore, there will be accumulation of heavy metal ions on the semipermeable membrane. Figure 2.1 shows the illustration of reverse osmosis technologies.

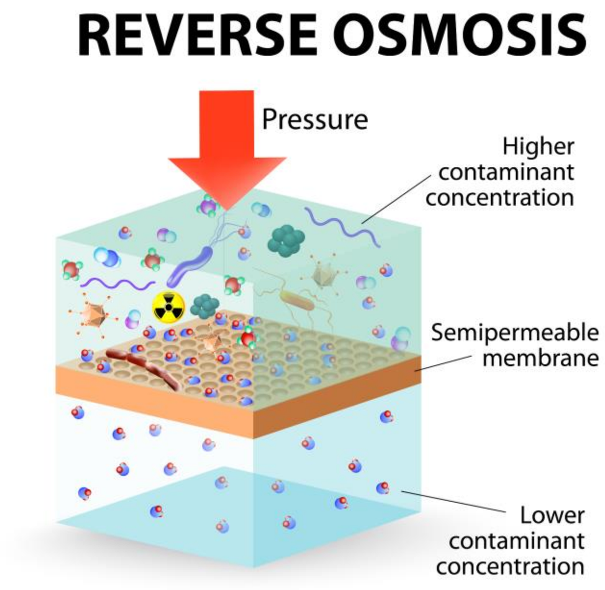

Figure 2.1: Reverse Osmosis Technologies (Higson, 2017).

Reverse osmosis is usually employed in seawater desalination and water purification. The water treated by reverse osmosis is environmentally friendly as it does not consume any chemicals and produce high water quality efficiently. However, according to Malaed and Ayoub (2010), membrane fouling is the main limiting factor of reverse osmosis application. The growth of microbes and scaling of dissolved organic substances will result in cakes formation on membrane, thus it needs to be replaced frequently. Besides, essential trace elements of human body will be removed by reverse osmosis (Jiang, et al., 2018). Furthermore, reverse osmosis is energy intensive process as external pressure source is required.

2.4.2 Chemical Precipitation

Chemical precipitation is the most common techniques adopted in the heavy metal ions removal (Gunatilake, 2015). Heavy metals are removed by addition of chemicals into the water to form precipitates to be separated from water. Chemical reagents such as alkali, sulphide, carbonates and coagulant will bond with dissolved metal ions and form an insoluble compound which is known as precipitate (Interstate Technology & Regulatory Council, 2010). For instance, common chemical reagents including sodium hydroxide, lime, limestone and alum. According to Wang, et al. (2005), chemical precipitation is usually followed by coagulation, clarification and filtration to separate the precipitates. Figure 2.2 illustrates the chemical precipitation treatment method.

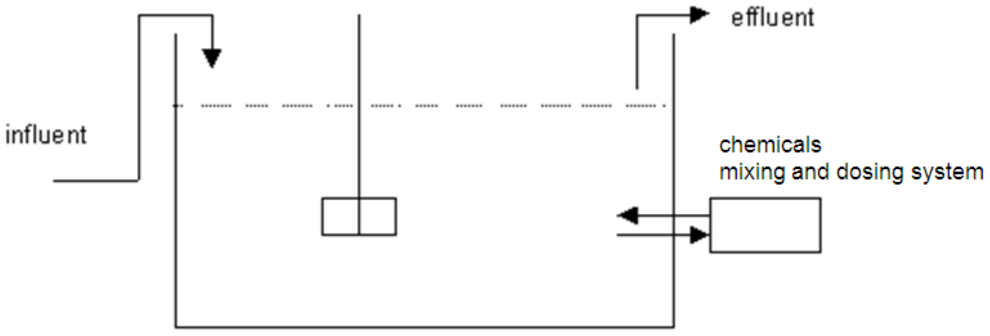

Figure 2.2: Chemical Precipitation Treatment Method (VITO, 2020).

Chemical precipitation is widely applied in water softening and stabilization, phosphate removal as well as heavy metals removal (Wang, et al., 2005). This technique is simple to operate and very efficient for metal elimination. However, there are some drawbacks of applying chemical precipitation. First, this process is expensive as large quantities of chemical reagents is consumed to remove the contaminants from wastewater. Besides, the physicochemical properties such as pH of effluent is required close monitoring for effective performance. If the concentration of metal ions is low, chemical precipitation would be ineffective in treating it. This treatment may also generate high number of solid sludges and hence requiring sludge treatment to handle and dispose of the waste (Crini and Lichtfouse, 2018). The processing cost to treat the solid wastes would be higher if the waste produced is hazardous.

2.4.3 Membrane Filtration

The working principle of membrane filtration is similar to reverse osmosis where a semipermeable membrane is utilized to separate the heavy metal ions or contaminants from water. However, membrane filtration can be operated without the application of external pressure to overcome the osmotic pressure of the solution. The dominant working principle in membrane filtration is the exclusion by particle size (Derek, 2017). Therefore, the efficiency of heavy metals removal is dependent on the pore size of membrane. Membrane filtration technique includes microfiltration, ultrafiltration and nanofiltration. Figure 2.3 shows different pore sizes of membrane filter.

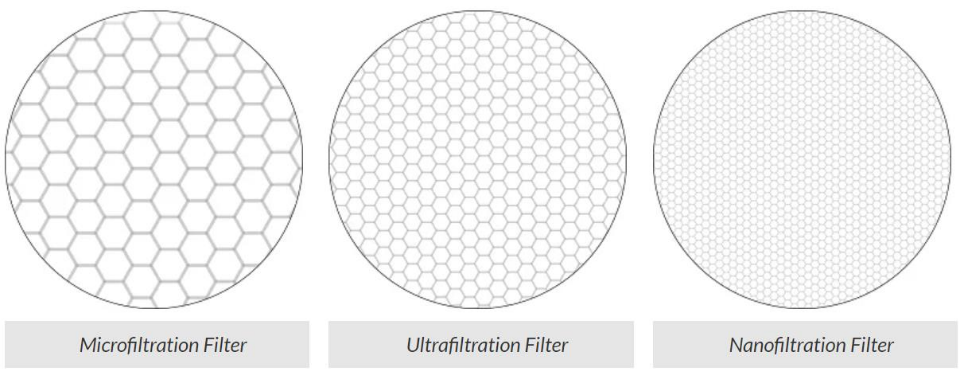

Figure 2.3: Membrane Filter with Different Pore Sizes (Derek, 2017).

Membrane filtration is the most common techniques that is implemented in wastewater treatment. It is flexible as specific filter membrane can be adopted according to size of particles going to be removed. Besides, it is highly efficient as the suspended solids can be completely removed from water. Nevertheless, the main obstacle of membrane filtration is membrane fouling. Membrane fouling will lead to pressure built up due to the accumulation of ions on membrane, thus frequent cleaning of membrane or the replacement of membrane is required. On top of that, waste will be generated during backwash and cleaning of membrane, thus a further waste treatment process is required (Igunnu and Chen, 2012).

2.4.4 Ion Exchange

Ion exchange is a process where undesirable heavy metal ions can be replaced by other similar charged ions in an equivalent amount (Gunatilake, 2015). Synthetic organic resin or zeolite which contain more desirable ions is utilized in ion exchange technology to facilitate the removal of specific heavy metals. During the water treatment process, influent with hazardous heavy metal ions come into contact with the ion exchange resin. According to Gunatilake (2015), water-insoluble ion exchange resin will absorb heavy metal ions from the solution and release desirable cations, for instance, sodium and hydrogen into the effluent. Figure 2.4 illustrates the typical configuration of ion exchange process for water treatment.

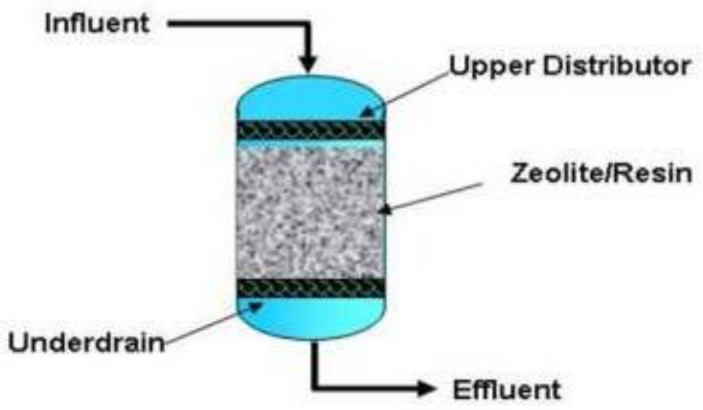

Figure 2.4: Ion Exchange Configuration (Reich, 2016).

Ion exchange is mostly applied for water softening, purification, dealkalization, deionization, and disinfection purposes. This is because it requires minimal energy and may operate continuously (Igunnu and Chen, 2012). However, there are some limitations in adopting this technology. Economic constraints is the main disadvantage of ion exchange technology. This is because the selective resin is expensive and high maintenance costs is required. Resin will be saturated by heavy metal ions rapidly and loss their activity, hence recharge or regeneration of resin is required. Next, the regeneration of resin is time-consuming. Resin beads might be fouled by particulates and organic matters. Besides, the metal ions removed from the solution might have secondary reactions and resulting in metal precipitation and clogging of reactor (Gunatilake, 2015).

2.4.5 Electrochemical Treatment

Electrochemical treatment is also known as electrolysis technology. An electrochemical treatment unit consists of electrodes, electrolytes and external power supply. In general, electrochemical process occurs where electricity is utilized for current to pass through a solution with heavy metals. When the current flows through, oxidation and reduction take place to precipitate out dissolved heavy metals as hydroxides (Kongsricharoem and Polprasert, 1995). According to Gunatilake (2015), electrochemical technologies include electrocoagulation, electrodeposition, electroflotation and electroxidation. Figure 2.5 illustrates the typical electrochemical technologies.

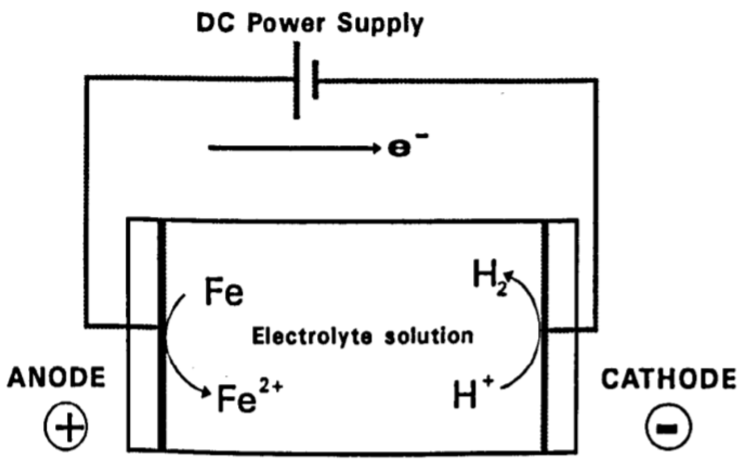

Figure 2.5: Schematic Diagram of Electrochemical Technologies (Kongsricharoem and Polprasert, 1995).

Electrochemical technology has high popularity in wastewater treatment due to its versatility and high efficiency. It is also environmentally friendly (Zhang, et al., 2013). Nevertheless, application of electrochemical treatment in removal of heavy metals require a large capital investment. Besides, it is energy intensive and is expensive as electricity supply is required (Azimi, et al., 2017). According to Gautam, et al. (2014), electrochemical treatment is ineffective in low metal ion concentrations of solution and large quantity of sludge will be generated. Hence, further waste treatment is required to treat the sludge. Electrochemical treatment will produce hydrogen gas in some reactions. Filtration is required to remove the flocs formed.

The working principles and limitations of these common heavy metals removal techniques are summarized in Table 2.4. It can be concluded that these conventional technologies are commonly expensive, energy intensive, require frequent maintenance on membrane and further sludge treatment as well as the capital investment is high. Therefore, it is necessary to seek for alternative options on the more technical and financially feasible methods for the heavy metals removal from water.

Table 2.4: Summary of Working Principles and Disadvantages of Conventional Heavy Metals Removal Technologies (Crini and Lichtfouse, 2018; Gunatilake, 2015; Gautam, et al., 2014; Igunnu and Chen, 2012).

Techniques	Working Principles	Disadvantages
Reverse Osmosis	Heavy metal ions removal from the solution by utilizing the semipermeable membrane and application of pressure.	• Membrane fouling. • Removal of essential trace elements of human body. • Energy intensive.
Chemical Precipitation	Addition of chemicals into the solvent to form solid precipitates to be separated from water.	• Expensive as large quantities of chemicals are required. • Physicochemical properties monitoring is required. • Ineffective in low metal ions concentration. • Solid sludges generated. • High processing cost to treat hazardous wastes.

Table 2.4: Continued.

Techniques	Working Principles	Disadvantages
Membrane Filtration	Heavy metal ions removal from the solution by utilizing the semipermeable membrane and exclusion by particle size.	• Membrane fouling. • Frequent cleaning or replacement of new membrane is required. Waste will be generated during backwash and cleaning of membrane.
Ion Exchange	Undesirable heavy metal ions can be replaced by other similar charged ions which is more desirable by utilizing a specialized resin.	• Expensive and high maintenance costs. • Rapid saturation of resins. • Regeneration of resin is time-consuming. • Resin fouling. • Occurrence of metal precipitation and clogging of reactor.

Table 2.4: Continued.

Techniques	Working Principles	Disadvantages
Electrochemical Treatment	Electricity is supplied to facilitate the removal of dissolved heavy metals in water.	• Large capital investments. • Energy intensive and high utilities cost to supply electricity. • Ineffective in low metal ions concentration. • Sludges are generated. • Hydrogen gas will be produced in some reactions. • Filtration is required to remove flocs.

2.5 Biosorption

Biosorption is a process where the heavy metals removal from the wastewater by utilizing biological material through metabolically passive or physico-chemical pathway (Ahalya, Ramachandra and Kanamadi, 2003). According to Podstawczyk, et al. (2015), biosorption is a process of contaminants binds onto the surface of biological materials which have chemical functional groups. It is considered as a promising method in treating aqueous solution which is highly polluted with heavy metals. As stated by Beni and Esmaeili (2019), biosorption reactions can be divided into four steps. First, the heavy metal ions are transferred from the aqueous solution to liquid boundary layer near the biosorbent. Next, the heavy metal ions move from the boundary layer to the surface of biosorbent and attach onto the biosorbent active sites to form a bond with functional groups on the active sites.

Biosorption is well-known for its high efficiency in metal accumulation and low-cost characterization. Besides, biosorption has several advantages over the conventional water treatment technologies. There is less chemical solvent utilization in biosorption, hence it can minimize the chemical or biological sludge produced as compared to chemical precipitation. Moreover, there is no additional nutrient requirement for biosorption to take place. The biosorbents which are utilized in biosorption can be regenerated and there is possibility to recover the metal accumulated on biosorbent (Ahalya, Ramachandra and Kanamadi, 2003).

According to Chen and Wang (2009), there are two modes of metal biosorption specifically, active mode and passive mode. Passive mode occurs when the cells of biological material used is metabolically inactive or dead. This process is energy independent or non-metabolism dependent and occurs chemically through functional groups on the cells or cell walls of the material. On the other hand, active mode by living cells is energy dependent or metabolism dependent which occurs by metal transport and deposition.

2.6 Mechanism of Biosorption

In this study, mechanisms of non-metabolism dependent biosorption is going to be investigated. According to Volesky and Holan (1995), the occurrence of biosorption of heavy metals is not solely based on a single mechanism but is contributed by different mechanisms that affected by biological material used, biomass origin, and biomass processing. The heavy metals biosorption is mainly taking place on cell surface through the interaction between heavy metals and biosorbent cell wall. The mechanisms involved in cell surface sorption consist of adsorption by electrostatic interaction, complexation, ion exchange, inorganic microprecipitation and redox reaction (Chen and Wang, 2009). These mechanisms can take place simultaneously. Figure 2.6 illustrates the major mechanisms involved in biosorption process.

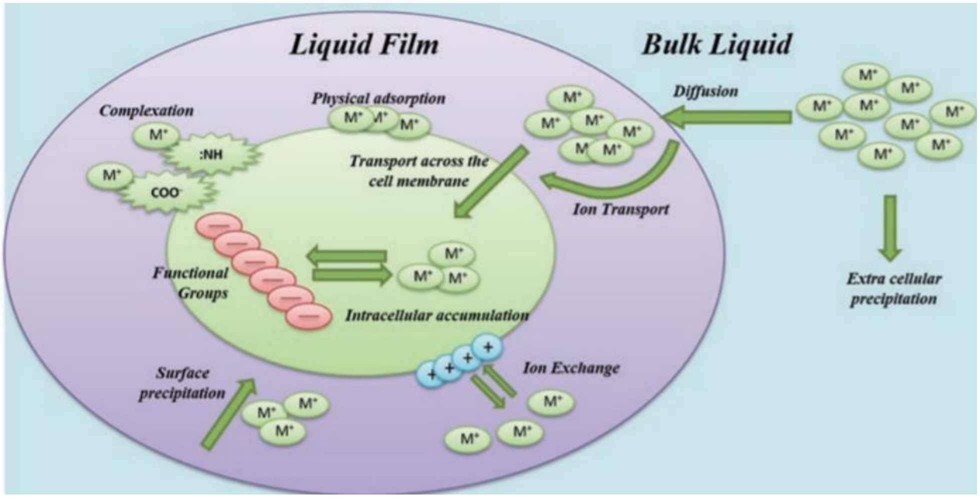

Figure 2.6: Mechanisms Occurs in Biosorption (Papirio, et al., 2017).

2.6.1 Adsorption

Heavy metal ions are attached to the biomass surfaces through the electrostatic interaction among the heavy metal ions and biosorbent surfaces. Physical adsorption occurs when there are weak attractive Van der Waals forces (Ahalya, Ramachandra and Kanamadi, 2003). This mechanism is immediate and reversible as heavy metal ions attached on the biosorbent surface can be recovered by utilizing other ions, acidic or alkaline solutions as efficient medium (Vijayaraghavan and Yun, 2008).

2.6.2 Complexation

Complexation refers to the formation of complexes on biosorbent cell surfaces through the interaction among heavy metal ions and active functional groups, include amino, phosphoryl, hydroxyl and carboxyl groups. Cations or central atoms will combine with molecules which contain free electron pairs or so called, ligand to form a complex through electrostatic or covalent bonding. Ligand contains multiple free electron pairs is known as multidentate ligand which able to join the metal cations together. Both protein and carbohydrate components of cell walls which has the amino, carboxyl, or hydroxyl groups are responsible in heavy metals binding (Chen and Wang, 2009).

2.6.3 Ion Exchange

Ion exchange mechanism in biosorption is important to remove heavy metal ions. According to Chen and Wang (2009), the release of cations from biosorbent will increase if it is reacted with aqueous solution containing heavy metal ions, indicating that ion exchange occurs when heavy metals contact with biosorbent cell surface. The heavy metal ions in aqueous solution will be exchanged with cations of polysaccharides which act as the basic building blocks available on the cell wall. For instance, the metal biosorption occurs where the cellular ions such as Ca^{2+}, K^{+}, Mg^{2+} or Na^{+} are released from the biosorbent cells and exchange with the counter ions such as Cd^{2+}, Cu^{2+}, Co^{2+}, and Zn^{2+} (Ahalya, Ramachandra and Kanamadi, 2003).

2.6.4 Precipitation and Redox Reaction

Precipitation occurs as a result of the chemical interaction among the heavy metals and the cell surface (Ahalya, Ramachandra and Kanamadi, 2003). The metal precipitates formed on biosorbent can be removed easily. Holan, Volesky and Prasetyo (1993) hypothesized that metal entrapment as insoluble microdeposits can contribute to high cadmium biosorption by using marine algae biomass. Besides, heavy metals ions can be oxidized or reduced to another oxidation state through redox reaction. There was a study proved that redox reaction involved in the biosorption where Cr^{6+} was reduced to Cr^{3+} by using dead fungal biomass of *Aspergillus niger* as stated by Chen and Wang (2009).

2.7 Biosorption Isotherm Models

The evaluation on biosorption capacity and tendency of biosorbent on metal uptake can be conducted based on variable biosorption isotherm models (Shen, et al., 2009). This evaluation is important to improve the performance of adsorption mechanism and design a more effective adsorption system (Ayawei, Ebelegi and Wankasi, 2017). There are two commonly employed biosorption isotherm models, scilicet Langmuir and Freundlich isotherms. By fitting the biosorption equilibrium data into both of these isotherm equations, the relationship between the quantity of metal uptake and the initial solute concentration in this study can be expressed.

2.7.1 Langmuir Isotherm Model

Langmuir adsorption is employed to depict gas-solid phase adsorption to compare and quantify the adsorption capacity of different biosorbents. Langmuir isotherm explains the surface coverage by achieving dynamic equilibrium through the balance between relative rate of adsorption and desorption (Ayawei, Ebelegi and Wankasi, 2017). There are few assumptions of Langmuir isotherm. According to Czepirski, Balys and Komorowska-Czepirska (2000), adsorption occurs at specific adsorption site of surface only and saturation is reached once the sites are fully occupied. Next, it is assumed that only single atom or molecule can adsorb onto an adsorption site. Moreover, the surface of all adsorption sites is assumed to be similar and the neighbouring atoms adsorbed do not interact with each other. Lastly, absence of phase transition is assumed. It was proposed by Langmuir (1918) which has a hyperbolic equation as presented in Equation 2.1 (Shen, et al., 2009).

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

where,

q_e = biosorption capacity per unit mass of biosorbent at equilibrium, mg/g

q_{max} = maximum theoretical biosorption capacity, mg/g

K_L = Langmuir equilibrium constant of adsorption capacity, L/mg

C_e = solute concentration at equilibrium, mg/L

2.7.2 Freundlich Isotherm Model

Freundlich isotherm is usually employed to describe adsorption process of organic and inorganic compounds on different adsorbents (Febrianto, et al., 2008). It assumes that the adsorption site is non-identical which is in contrast to Langmuir isotherm. Besides, this isotherm defines that the active sites and energy are distributed exponentially (Ayawei, Ebelegi and Wankasi, 2017). Hence, it is only applicable for the concentration with low to intermediate ranges (Liu and Liu, 2007). The empirical relation between the biosorption capacity and solute concentration as proposed by Freundlich (1907) is expressed in Equation 2.2 (Shen, et al., 2009).

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

where,

q_e = biosorption capacity per unit mass of biosorbent at equilibrium, mg/g

k_F = Freundlich constant of adsorption capacity

C_e = solute concentration at equilibrium, mg/L

n_F = Freundlich constant of adsorption intensity

2.8 Biosorption Kinetic Models

Biosorption kinetics is important to estimate the optimal operating conditions to achieve efficient biosorption. Generally, two kinetic models, scilicet pseudo-first-order and pseudo-second-order equations are employed to explain biosorption data obtained under the condition which is nonequilibrium (Shen, et al., 2009). Most of the researchers employed both kinetic models parallelly and usually one of them is claimed to be better based on the marginal difference in correlation coefficient (Liu and Liu, 2007). These kinetic equations relate the adsorption rate to the metal uptake quantity by biosorbent (Rudzinski and Plazinski, 2006).

2.8.1 Pseudo-First-Order Model

Pseudo-first-order model is also considered as Lagergren equation which was proposed by Lagergren (1898) (Rudzinski and Plazinski, 2006). It is widely employed to describe the kinetics of metal uptake at solid-liquid interface. It was associated with single site occupancy adsorption (Rudzinski and Plazinski, 2006). According to Liu and Liu (2007), this equation is corresponding to the linear driving force concept. This model is represented linearly by Equation 2.3 (Huang, et al., 2019).

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{2.3}$$

where,

q_e = biosorption capacity per unit mass of biosorbent at equilibrium, mg/g

q_t = biosorption capacity per unit mass of biosorbent at time (t), mg/g

k_1 = first order rate constant, min^{-1}

t = time, min

2.8.2 Pseudo-Second-Order Model

Pseudo-second-order model was offered by Blanchard, et al. (1984) (Liu and Liu, 2007). Chemisorption, complexation, chelation or coordination and diffusion are the rate limiting steps indicated by pseudo-second-order kinetic model in metal biosorption (Febrianto, et al., 2008). This kinetic model becomes popular to be employed since Ho and McKay (1999) reported that the best correlation of experimental data can be obtained by using pseudo-second-order reaction kinetics (Simonin, 2016). This model is described linearly by Equation 2.4 (Huang, et al., 2019).

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

where,

q_e = biosorption capacity per unit mass of biosorbent at equilibrium, mg/g

q_t = biosorption capacity per unit mass of biosorbent at time (t), mg/g

k_2 = second order rate constant, $\frac{g}{mg \cdot min}$

t = time, min

2.9 Summary of Literature Review

There is large amount of research on the biosorption on removal of cationic contaminants have been published. These research have been provided a better understanding on metal biosorption. In conjunction with the human health hazards, heavy metal pollution in water need to be overcomed. Removal of cadmium ion is selected to be investigated in this study because it is considered as a hazardous element in potable water. By comparing with conventional treatment technologies for water, biosorption is considered as the most cost-effective technology where it adopts biosorbent which is economic viable, sustainable and environmentally friendly. Research on different types of biosorbents especially fruit biosorbents have been widely utilized to remove different heavy metal ions were investigated. However, it is necessary to continue looking for more suitable and promising biosorbent from the large pool of readily available and cheap biological materials. For this reason, the study of removal of cadmium contaminant through biosorption by utilizing biosorbent is important. Therefore, the cadmium biosorption by different types of biosorbent and the effect of operating conditions on the biosorption performance are required to be evaluated.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Overall Research Methodology and Flow Diagram

In general, the overall literature review in this study was conducted by narrative review approach. The review utilises qualitative research method which aims to summarize, analyse and interpret on the research works that had been done by other researchers. Basically, four main phases were carried out to complete this research work. First, sourcing for literature review was conducted through different platforms to obtain the relevant information on the biosorbents that had been used in the removal of cadmium from water. Then, the literatures were screened according to the pre-set criteria and were sorted using Excel database. After that, the relevant experimental data were extracted from the literatures to evaluate the best adsorption uptake of the biosorbents, isotherm and kinetic studies, effect of different operating parameters on biosorption performance as well as the removal mechanism and functional groups that were responsible for the cadmium biosorption. Lastly, the suitability of avocado peel as biosorbent was analysed by comparing with the extracted data. The presentation of literature review was done using the narrative analysis method. Figure 3.1 delineates the flow diagram of literature review in this study.

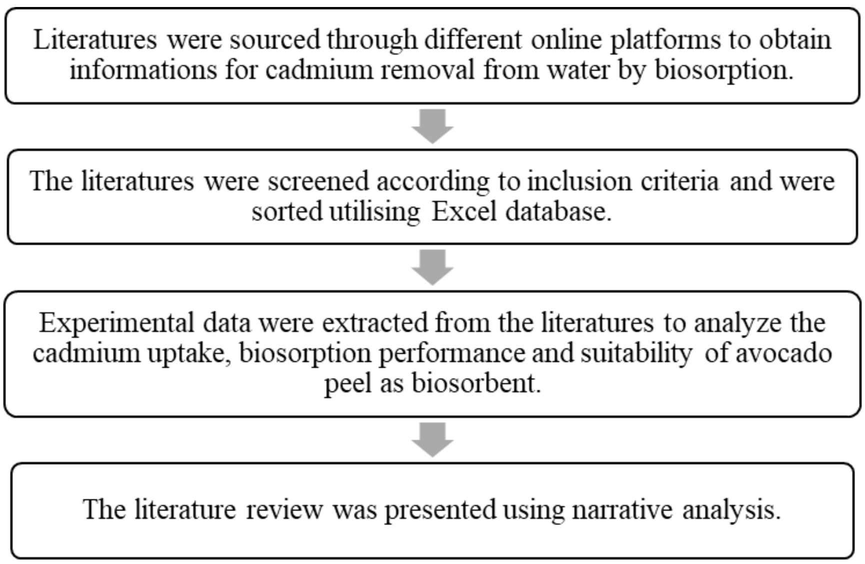

Figure 3.1: Flow Diagram of Overall Research Methodology.

3.2 Sources of Literature Review

Since this research work will be conducted by using narrative review approach, a number of literatures are required to accomplish the review works. Information have to be collected to provide a deep insights and understandings on the topic of interest. There are three main categories of literature review sources which are primary, secondary and tertiary sources.

Primary sources of literature review are the original version of the research works which provides preliminary data and raw evidence on a specific topic. Primary sources include reports of original experiment, empirical studies, interview transcripts, newspapers, and government documents (Streefkerk, 2018). On the other hand, secondary sources are the written sources that are produced from the summarization, analysis and interpretation of the primary sources. Secondary sources consist of books, review articles and journals (Streefkerk, 2018). Tertiary sources such as encyclopedias, bibliographies and handbooks are the sources that created by compiling and restructuring the information obtained from the primary and secondary sources.

Numerous literatures were sourced through various online platforms such as UTAR library online databases, ResearchGate, Springer and ScienceDirect and other e-journals as well as scholarly article publications. The main sources of literature review involved in this study were the secondary sources such as review articles, e-journals and e-books.

3.3 Screening for Inclusion and Evaluating the Quality of Primary Studies

Since numerous literatures can be obtained through different online platforms, the screening for inclusion of literatures has to be carried out to narrow down the scope and include only those appropriate, important and useful databases for literature review in this study. In this case, few inclusion criteria had been determined before conducting the review works. This is one of the most important steps when conducting literature review to decide the quality of primary studies.

The first criteria that going to be taken into consideration is the year of publication of the literatures. Only the literatures which are published within the past 12 years were included. This is to make sure that the information obtained are updated and more relevant to the latest studies. Besides, the keywords that were used to search for the literatures must include the terms of removal or biosorption, cadmium and aqueous solution. Therefore, a complete and specific information regarding on the biosorbents used to remove cadmium through biosorption could be obtained to draw a more accurate conclusion in this study. Furthermore, the literatures which were not published in English will be excluded from the review works. Lastly, it was important to include only those literatures with proper citation and references provided. This is to ensure that the research works that are conducted by the researchers were based on trusted source of studies.

Next, thorough review on the literatures was conducted. The abstracts of each literature were read to understand the scope of the content. After that, the more relevant literatures were selected and prioritized to further review and analysis. Then, the screening for the text from the literatures was carried out by highlighting the content to be used later for presenting the literature review in this report. This can help to evaluate the quality of the primary studies by extracting the useful content.

After conducting the screening for inclusion and evaluating the quality of primary studies, the appropriate and useful literatures that are utilized for the review works were sorted in an Excel database, as shown in Figure 3.2. A few key element parameters were included in the database such as name of author, year of publications, biosorbents investigated, operating parameters, the isotherm and kinetic studies as well as the functional groups involved in the removal process. As such, it was more convenient and easier to trace the key elements of the literatures in the report writing.

	A	B	C	D	E	F	G	H	I	J	K
1	Name of Author	Year of Publications	Biosorbents/Adsorbent Used	Removal Efficiency (mg/g)	pH	Volume of Metal Solution	Biosorbent Dosage	Temperature (deg C)	Contact Time	Isotherm Study	Kinetic Study
2	Tanasal, La-Nafie and Taba	2015	Dragonfruit Peel	36.5	5	50 mL	0.2 g		20 mins	Langmuir	
3	Gillbert, et al.	2011	Defatted Papaya Seed	1000	5	50 mL	0.5 g		20 mins	Freundlich	Pseudo-second
4	Sanusi, Umar and Abdullahi	2015	Carica Papaya Seed	63.58	5	20mL	1.0g	35	60 mins	Langmuir	Pseudo-second
5				90.95	5	20mL	1.0g	55	60 mins	Langmuir	Pseudo-second
6	Lakshmipathy, Vinod and Sarada	2013	Watermelon Rind	63.29	4.9	20mL	0.03 g		30 mins	Langmuir	Pseudo-second
7	Saikaew and Kaewsarn	2009	Durian Peel	18.55	5	100 mL	0.1g	25	1440 mins	Langmuir	
8			Pomelo Peel	21.83	5	100 mL	0.1g	25	1440 mins	Langmuir	
9			Banana Peel	20.88	5	100 mL	0.1g	25	1440 mins	Langmuir	
10	Iqbal, Saeed and Zafar	2009	Mango Peel	68.92	5	100 mL	0.25g		60 mins	Langmuir	Pseudo-second
11	Chen, et al	2018	Litchi Peel	230.5	5	100 mL	0.1 g	25	480 mins	Langmuir	Pseudo-second
12			Orange Peel	170.3	5	100 mL	0.1 g	25	480 mins	Langmuir	Pseudo-second

Figure 3.2: Excel Sheet to Sort the Literatures.

Also, Citavi referencing tool was employed for referencing the literatures used in the review work. This ensured the correct format was used for the referencing and the database can be maintained systematically.

3.4 Extract and Analyse Data

After the thorough review of literatures was completed, the important data will be extracted from the literatures. First and foremost, the relevancy of the data to the topic of interest was determined before extracting the information to avoid unreliable and inappropriate results which may lead to an inaccurate data analysis.

According to the objectives of this research work, the experimental data of adsorption uptake of different types of biosorbents to remove cadmium from water as well as their isotherm and kinetic studies were extracted and collected using Microsoft Excel. This was to achieve the first objectives of the study which is to evaluate the use of different types of biosorbent to remove cadmium from water.

Besides, the experimental data on the effect of three different operating parameters, namely pH, solution to biosorbent dosage ratio, and contact time were also extracted from the literatures so that the biosorption performance can be evaluated by utilizing the graphical method to accomplish the second objective of the study. As such, the optimum operating condition for the biosorbents to remove cadmium from water effectively was predicted.

Moreover, the information on the removal mechanism and functional groups that are responsible for cadmium biosorption were also identified from the literatures based on the characterisation studies that had been reported by other researchers using four instruments which were Brunauer-Emmett-Teller (BET), Energy Dispersive X-ray (EDX), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).

The analysis of data was further conducted to evaluate the theories and viewpoints provided by other researchers on the adsorption uptake using different types of biosorbents, optimum biosorption operating conditions along with the responsible functional groups in the biosorption process. Last but not least, the suitability of avocado peel as the biosorbent for removing cadmium from water was predicted based on the interpreted data.

3.5 Presentation of Literature Review

There are several ways to present a literature review, such as grounded theory, narrative analysis, meta-ethnography, frequency analysis and meta-analysis. In this study, narrative analysis is a qualitative research employed to synthesize the qualitative evidence on the feasibility of cadmium removal by utilizing biosorbents. Dialogical narrative analysis was implemented in presenting the findings for this research work. There are totally six steps to conduct the dialogical narrative analysis (Smith, 2016), namely: getting the model, getting to grip with the model, opening up analytical dialogue further, pulling the analysis together, build a typology and represent the results.

3.5.1 Getting the Model

The narrative analysis is started with getting the conceptual model, which is the content of literature reviews based on the topic of interests decided. After obtaining and screening the literatures from different platforms with the inclusion criteria, data transcription will be carried out where questions will be asked so that analytical thoughts can be stimulated to include and transcribe the data or content for report writing. For examples: “which biosorbents are more popular to be used?”, “do they require any surface modification to carry out the biosorption process?” and “how the biosorbents carry out the biosorption process?”. While conducting data transcription, the data transcribed was written down to ensure that the ideas for writing the report can be discovered continuously and relevant information can be assessed immediately throughout the literatures (Smith, 2016).

3.5.2 Getting to Grip with the Model

This is the step which involves the reading and re-reading of the information in the literatures as to familiarize with the content of the literatures, hence enhance the understanding on the content of literatures assessed. First, the outline will be identified by looking for the summary of the literatures which highlight the key elements of the overall literatures.

After that, the content of the literature will be identified to understand narrative themes of the literatures. Narrative theme is the pattern that visualize the flow of the content. In this case, narrative theme for the primary sources will be identified to visualize the flow of the research works conducted by the other researchers to investigate the biosorption of cadmium by utilizing adsorbents or biosorbents. In this study, narrative themes can be classified into few main themes such as adsorption uptake, isotherm study, kinetic study and characterisation study.

Next, the structure of the literature was identified. It is important to identify the structure because it indicates the direction of the research works, the limitations of the research work and the methods used to achieve the objectives of the study (Smith, 2016).

3.5.3 Opening Up Analytical Dialogue Further

Before starting to write the report for literature review, questions were asked to have a better understanding of the model. This is useful to consider what content can be included in a report writing and why previous researchers exclude from their write up. There were six categories of questions involved in this stage which were resource questions, circulation questions, connection questions, identity questions, body questions and function questions. Table 3.1 shows the sample of the questions that were made in this study based on these categories.

Table 3.1: Possible Questions Involved in Presentation of Literature Review.

Categories of Questions	Sample Questions
Resource Question	1. Which adsorbents or biosorbents have been used by the researchers to conduct the research? 2. What are the handling methods that are applied to the preparation of adsorbents or biosorbents? 3. Any surface modification was done for the biosorbents?
Circulation Question	1. What are the objectives that are tried to achieve in this study? 2. What are the scopes that are included in the research carried out by the previous researchers?
Connection Question	1. How to relate the results of previous studies with this research work?
Identity Question	1. How was the researchers investigate the adsorption uptake of biosorbents? 2. How was the researchers identify the functional groups involved in the biosorption of cadmium?
Body Question	1. What have the previous researchers done to carry out the evaluation of biosorbents? 2. How to analyse on the effectiveness of the biosorbents to remove cadmium? 3. How is the data interpretation been carried out?
Function Question	1. What is the maximum adsorption uptake of the biosorbents? 2. How is the biosorption performance affected by different operating parameters? 3. What are the functional groups responsible to remove the cadmium?

3.5.4 Pulling the Analysis Together

This step can be conducted in a variety of ways. After extract the relevant information based on the questions formulated in previous step, the data are tabulated accordingly and analysed accordingly. In this study, the statistical and graphical methods were applied to analyse all the data obtained from the literatures by identifying the relationship between them, so that a typology can be built.

3.5.5 Build a Typology

A typology can be built by reading through the analysis of the studies which gathers all the results. Therefore, a list of specific content that is to be written in the report can be determined. This process was conducted via three steps. First, the flow of the write up and the impact that might be bring to this research work was drafted. Then, the content of the report was improved accordingly. Finally, report writing was structured according to the typology built, edited and revised to produce a good quality of report.

3.5.6 Represent the Results

The last step of narrative analysis is to present the literature review work by writing up the report. The results and discussion of the report were started with an introduction on the adsorbents and biosorbents that have been applied in previous studies. Next, all the findings were discussed and interpretated around the typology built in Section 3.5.5 so that the report was not biased from the objectives of the research. Lastly, a conclusion of this research work on the technical feasibility of biosorption to remove cadmium from water and recommendations was provided to improve the research work in future.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Types of Biosorbents used for Cadmium Removal

Research on metal biosorption from water became active recently with various biosorbents of different origins. From published research journals and related references, the biomass that were easily available were adopted as the potent biosorbent materials. Living microorganisms have the capability to accumulate the cadmium ion from wastewater on account of the active metabolism of living cells. On the other hand, dead microbial biomass can also attach the cadmium ions passively through different physicochemical mechanisms which had been proven by the other researchers.

In this study, few main categories of the tested biosorbents during the past 12 years were reviewed, which consist of bacteria, fungi, algae and agricultural wastes. In general, the biosorbents have different adsorption uptake, as the biosorption process is not only affected by the chemical composition or the type of the biomass, but also the solution chemistry and external physicochemical factors.

In addition, the biosorption capacity and the tendency of biosorbent on cadmium uptake were evaluated based on the isotherm models specifically Langmuir and Freundlich models. Furthermore, the mechanisms that are responsible for cadmium biosorption have also been investigated where they may be a single mechanism involved or the combination of cadmium adsorption, complexation, electrostatic interaction, ion exchange and microprecipitation (Chen and Wang, 2009). As such, pseudo-first and pseudo-second order were exercised to portray the kinetics of cadmium uptake.

4.1.1 Living Microorganisms

Living microorganisms such as bacteria, algae and fungi are easily available and this gives broader choices for the use of biosorbent in cadmium removal. Besides, the byproduct biomass of fungi from largescale fermentation processes can also be used as the biosorbent. Different methods had been applied by different researchers in looking for the feasibility of microorganisms as biosorbents, such as directly used the available raw biomass, isolation of microbes' strains, and modification of the cell surface thermally and chemically. This leads to the variation of the biosorption results.

Bacteria are the most abundant living microorganisms that had been investigated and they were known to have high capacity to accumulate the metallic element in early 1980 (Chen and Wang, 2009). Bacteria were adopted as biosorbents due to their high availability, small size as well as capability to cultivate under controlled conditions and environmental situations. According to Chen and Wang (2009), bacteria species such as *Aeromonas caviae, Enterobacter sp., Pseudomonas sp., Staphylococcus xylosus* and *Streptomyces* have been tested for the cadmium removal. The reported range of cadmium uptake are from 46.2 mg/g to 278 mg/g, in which *Pseudomonas sp.* shows the highest cadmium uptake, whereas, *Enterobacter sp.* shows the lowest cadmium uptake rate.

On the other hand, fungi such as yeast, molds and mushrooms were also widely applied as the biosorbent for cadmium uptake due to their ability to attach the metallic elements. Fungi are found abundant in nature and they play important roles in food and beverage industries for fermentation processes. This is because a range of morphologies especially the complex macroscopic fruiting bodies are discovered from the unicellular yeasts to polymorphic and filamentous fungi (Chen and Wang, 2009). Furthermore, filamentous fungi and yeasts are cultivated easily, which can generate high supply of biomass and able to be controlled morphologically and genetically.

Filamentous fungi such as raw *Aspergillus niger*, *Penicilliun sp.* and *Penicillium canescens* had been employed to extract cadmium from the aqueous solutions which has the cadmium biosorption capacity of 1.31 mg/g, 3 mg/g and 102.7 mg/g respectively (Chen and Wang, 2009). The cadmium uptake by the waste baker's yeast treated by ethanol shows a cadmium uptake of 15.6 mg/g (Goksungur, et al., 2005).

Algae are conspicuous in the research findings for new biosorbent materials development because of their high availability in marine and high sorption uptake capacity. The algal group can be classified into various group include brown algae (Phaeophyta), red algae (Rhodophyta), green algae (Chlorophyta), golden-brown algae or diatoms (Chrysophyta) and et cetera. As reported by Chen and Wang (2009), the cell walls of algae are more complex as compared to bacteria or fungi. For example, the cell wall of brown algae includes three components which are alginic acid as polymer, cellulose as structural support as well as sulphated polysaccharides. In contrast, the cell wall of red algae also contains cellulose, but the sulphated polysaccharides are made up of galactanes which helps in the biosorption process. Furthermore, cell walls of green algae are comprised mostly of cellulose, and proteins that are bonded to polysaccharides to produce glycoproteins. The difference in cell wall structure and composition was found to highly affecting the biosorption uptake.

According to Chen and Wang (2009), the algae adsorption uptake for cadmium is relatively lower as compared to other heavy metals where there are 12.57 % of marine microalgal strains resistant to cadmium ions. However, the marine green algae, *Chlorella sp.* manifested the maximum cadmium removal at 37.0 mg/g. In addition, it was also reported that cadmium was adsorbed faster by the dried algal cells as compared to living cells, with an adsorption uptake of 91.0 mg/g (Chen and Wang, 2009). According to Nessim, et al. (2011), the cadmium uptake by marine algae such as brown algae (*Sargassum sp.*) are 2 times higher of efficiency as compared to green algae (*Ulva fasciata*).

In view of the biosorption process that includes predominantly the sequestration of cell surface, the alteration on cell wall of microbes can significantly enhance the biosorption performance. Several physical and chemical treatments could be applied to alter the biomass surface characteristics by either removing certain groups or exposing more sites for binding. The physical treatments include thawing, heating and drying, whereas, chemical treatments include acid or alkali treatment, cross-linking with organic solvents, and washing the biomass with detergents. For example, cadmium biosorption by using *Aspergillus niger* biomass was studied. The raw *Aspergillus niger* biomass was pretreated chemically by using sodium hydroxide and the result showed a significant improvement from 1.31 mg/g to 3.43 mg/g in the cadmium biosorption (Chen and Wang, 2009). This is because the uncomfortable growth conditions for living microorganisms might influence their cell components or changes in the cell surface compositions that affect their biosorption potential directly, as stated by Chen and Wang (2009).

4.1.2 Agricultural Waste Biosorbent

Agricultural waste is of interest to be applied as biosorbent recently due to its low-cost characterisation. Agricultural waste is generated from agricultural or domestic activities and they are normally disposed to landfill. Agricultural waste includes plant materials, food wastes such as corn cob and coffee ground, as well as fruit peels, the most common biosorbents that are tested by researchers as they are readily available, cheap, environmentally friendly and easily to handle (Asuquo and Martin, 2016; Cheraghi, Ameri and Moheb, 2015; Lakshmipathy, Vinod and Sarada, 2013). They can even be recycled and reused after they are rejuvenated once the heavy metal ions are desorbed (Othman, Mohd-Asharuddin and Azizul-Rahman, 2013).

The agricultural wastes have to be prepared and treated before being utilized as biosorbents. In general, the agricultural wastes need to be washed to remove all the impurities and contaminants before they are dried to remove the moisture content. After that, they are cut and sieved to have a uniform size of particles and amplify the surface area for the biosorption process. The smaller the particle size, the higher the cadmium uptake rate as larger surface area is provided (Cheraghi, Ameri and Moheb, 2015; Gilbert, et al., 2011; Saikaew and Kaewsarn, 2009).

The researches have proven that both natural or modified form of agricultural wastes, are remarkably efficient in adsorbing the cadmium ions from aqueous solution. This is because agricultural wastes, especially the plant materials are rich in nutrient and contain large amount of fibers which comprised of cellulose, hemicellulose and lignin, as well as a variety of functional groups which helps in the biosorption process happens on the surface (Cheraghi, Ameri and Moheb, 2015).

Numerous potential agricultural wastes were employed for the cadmium removal such as natural and modified forms of rice husk, rice polish, black gram husk, walnut shells, peanut hulls, green coconut shells and hazelnut shells

(Cheraghi, Ameri and Moheb, 2015; Kumar and Bandyopadhyay, 2006; Kurniawan, et al., 2006).

4.1.3 Adsorption Uptake of Biosorbents

In this section, the cadmium uptake performance of various biosorbents was reviewed based on the published references. There are two main methods to carry out the biosorption process which are batch scale study using shake flask and continuous study using packed bed column reactor. However, from the large quantity of published reviews, it was observed that the researchers usually conducted the biosorption process through batch experiment by using the shake flask. Adsorption uptake or cadmium biosorption capacity per unit mass of biosorbent at equilibrium for different biosorbents at their different operating conditions are listed in Table 4.1.

Table 4.1: Comparison of Different Biosorbents and Adsorbent Studied in Cadmium Ion Removal.

Biosorbents	**Types of Biosorbents**	**pH**	**Biosorbent Dosage (g)**	**Contact Time**	**Cadmium Uptake (mg/g)**	**References**
Banana Peel	Agricultural Waste	5.0	0.1	24 hours	20.88	Saikaew and Kaewsarn, 2009.
		5.0	0.1	8 hours	98.40	Chen, et al., 2018.
Carica Papaya Seed		5.0	1.0	60 mins	63.58 (at 35℃) 90.95 (at 55℃)	Sanusi, Umar and Abdullahi, 2015.
Durian Peel		5.0	0.03	24 hours	18.55	Saikaew and Kaewsarn, 2009.
Defatted Papaya Seed		5.0	0.5	20 mins	1000	Gilbert, et al., 2011.
Dragonfruit Peel		5.0	0.2	20 mins	36.50	Tanasal, La-Nafie and Taba, 2015
Litchi Peel		5.0	0.1	8 hours	230.5	Chen, et al., 2018.
Mango Peel		5.0	0.25	60 mins	68.92	Iqbal, Saeed and Zafar, 2009.
Orange Peel		5.0	0.1	8 hours	170.3	Chen, et al., 2018.
Pomelo Peel		5.0	0.1	24 hours	21.83	Saikaew and Kaewsarn, 2009.
Pomegranate Peel		5.0	0.1	8 hours	132.5	Chen, et al., 2018.
Watermelon Rind		4.9	1.0	30 mins	63.29	Lakshmipathy, Vinod and Sarada, 2013.

Table 4.1: Continued.

Biosorbents	Types of Biosorbents	pH	Biosorbent Dosage (g)	Contact Time	Cadmium Uptake (mg/g)	References
Biomass of Oryza Sativa	Agricultural Waste	6.0	10	30 mins	4.47	Fawzy, et al., 2016.
Chestnut Shell		6.06	2.0	4.43 hours	51.28	Huang, et al., 2018.
Corn Cob		5.0	0.5	30 mins	21.48	Tan, et al., 2011.
Coffee Grounds		7.0	9.0	2 hours	15.65	Azouaou, et al., 2010.
Ficus Carica		5.0	0.5	80 mins	30.31	Farhan, Al-Dujaili and Awwad, 2013.
Rice Husk		5.0	0.5	30 mins	29.67	Tan, et al., 2011.
Sesame		6.0	0.1	30 mins	84.74	Cheraghi, Ameri and Moheb, 2015.
Strychnos Potatorum Seeds		5.0	0.2	30 mins	200.0	Kumar, et al., 2012.
Sweet Potato Peel		7.0	2.0	3 hours	18.8	Asuquo and Martin, 2016.
Tea Waste		5.0	0.5	90 mins	0.497	Ghasemi, Mafi Gholami and Yazdanian, 2016.

Table 4.1: Continued.

Biosorbents	**Types of Biosorbents**	**pH**	**Biosorbent Dosage (g)**	**Contact Time**	**Cadmium Uptake (mg/g)**	**References**
Opuntia Albicarpa L. Scheinvar	Agricultural Waste	4.0	2.0	15 mins	0.155	Beltrán-Hernández, et al., 2015.
Unmodified Rice Straw		5.0	1.0	3 hours	13.9	Ding, et al., 2012.
Wheat Stem		5.0	0.5	30 mins	26.07	Tan, et al., 2011.
Water Hyacinth (Eichhornia Crassipes)		6.0	0.1	150 mins	104.0	Murithi, et al., 2014.
Residue of Padina Gymnospora Waste	Algae	6.2	0.05	3 hours	96.46	Mohamed, et al., 2019.
Ulva Fasciata		4.0	1.0	4 hours	49.90	Nessim, et al., 2011.
Immobilized Microcystis Aeruginosa	Bacteria	6.0	2.0	3 hours	98.38	Wang, et al., 2014.
Recombinant Escherichia Coli with 33wt% Biomass		5.0	10	24 hours	4.290	Kao, et al., 2009.

Table 4.1: Continued.

Biosorbents	Types of Biosorbents	pH	Biosorbent Dosage (g)	Contact Time	Cadmium Uptake (mg/g)	References
Aspergillus Niger	Fungi	6.5	1.33	72 hours	5.580	Munawar, et al., 2018.
Bamboo Charcoal	Activated Carbon	8.0	0.5	6 hours	12.08	Wang, Wang and Ma, 2009.
Biochars from Eichornia Crassipes		5.0	0.01	5 hours	49.84 (WH-300) 36.90 (WH-500) 25.83 (WH-700)	Li, et al., 2016.
Engineered Biochar Derived from Potassium Permanganate ($KMnO_4$) Treated Hickory Wood		6.0	0.05	24 hours	28.10	Wang, et al., 2015.
Pinus Halepensis Sawdust		9.0	10	30 mins	5.36	Semerjian, 2010.
Surface-modified Activated Carbon		9.0	0.1	2 hours	0.96	Liang, Liu and Zhang, 2016.

As shown in Table 4.1, adsorption experiments can be conducted using different types of biosorbent material include agricultural waste, algae, bacteria, fungi as well as activated carbon. The cadmium uptake is in a trend of agricultural waste > algae > bacteria > activated carbon > fungi. It is observed that utilizing agricultural waste as the adsorbents can provide a high and promising biosorption efficiency where the cadmium uptake is ranged from 0.155 mg/g to 1000 mg/g. Among the agricultural waste, defatted papaya seed shows the highest adsorption uptake of 1000 mg/g, which indicating that it has higher affinity in removing cadmium ions from water. Next, the maximum adsorption uptake by algae is ranged from 49.90 to 96.46 mg/g, followed by bacteria which shows an adsorption uptake of 4.29 mg/g to 98.38 mg/g. The adsorption uptake that can be achieved by activated carbon is reported from 0.96 mg/g to 49.84 mg/g only as shown in Table 4.1, Therefore, the cadmium uptake by activated carbon is relatively lower than algae and bacteria. Lastly, fungi are the least promising biosorbent in removing cadmium from water as it can only provide an adsorption uptake of 5.580 mg/g after 72 hours of contact time.

4.1.4 Isotherm and Kinetic Studies

Langmuir and Freundlich isotherm models are widely adopted in the reviewed literatures to describe the cadmium adsorption mechanisms. On the other hand, pseudo-first and pseudo-second order kinetic models are also widely exercised to determine the mechanism of biosorption and the rate limiting steps that affecting the biosorption rate of cadmium. The isotherm and kinetic studies of different biosorbents in cadmium removal are tabulated in Table 4.2.

Table 4.2: Comparison of Isotherm Study and Kinetic Study of Different Biosorbents Studied in Cadmium Removal.

Biosorbents	Types of Biosorbents	Isotherm Study	Kinetic Study	References
Banana Peel	Agricultural Waste	Langmuir	Pseudo-second Order	Saikaew and Kaewsarn, 2009. Iqbal, Saeed and Zafar, 2009.
Carica Papaya Seed		Langmuir	Pseudo-second Order	Sanusi, Umar and Abdullahi, 2015.
Defatted Papaya Seed		Freundlich	Pseudo-second Order	Gillbert, et al., 2011.
Dragonfruit Peel		Langmuir	-	Tanasal, La-Nafie and Taba, 2015.
Durian Peel		Langmuir	-	Saikaew and Kaewsarn, 2009.
Litchi Peel		Langmuir	Pseudo-second Order	Chen, et al, 2018.
Mango Peel		Langmuir	Pseudo-second Order	Chen, et al, 2018.
Orange Peel		Langmuir and Freundlich	Pseudo-second Order	Chen, et al, 2018. Jha and Kumari, 2020.
Pomelo Peel		Langmuir	-	Saikaew and Kaewsarn, 2009.
Pomegranate Peel		Langmuir	Pseudo-second Order	Chen, et al, 2018.
Watermelon Rind		Langmuir	Pseudo-second Order	Lakshmipathy, Vinod and Sarada, 2013.

Table 4.2: Continued.

Biosorbents	Types of Biosorbents	Isotherm Study	Kinetic Study	References
Biomass of Oryza Sativa	Agricultural Waste	Langmuir	Pseudo-second Order	Fawzy, et al., 2016.
Chestnut Shell		Langmuir	Pseudo-second Order	Huang, et al., 2018.
Corn Cob		Langmuir	Pseudo-second Order	Tan, et al., 2011.
Coffee Grounds		Langmuir	Pseudo-second Order	Azouaou, et al., 2010.
Ficus Carica		Langmuir	Pseudo-second Order	Farhan, Al-Dujaili and Awwad, 2013.
Rice Husk		Langmuir	Pseudo-second Order	Tan, et al., 2011.
Sesame		Langmuir	Pseudo-second Order	Cheraghi, Ameri and Moheb, 2015.
Strychnos Potatorum Seeds		Langmuir	Pseudo-second Order	Kumar, et al., 2012.
Sweet Potato Peel		Langmuir	Pseudo-first Order	Asuquo and Martin, 2016.
Unmodified Rice Straw		Langmuir	Pseudo-second Order	Ding, et al., 2012.
Wheat Stem		Langmuir	Pseudo-second Order	Tan, et al., 2011.
Water Hyacinth (Eichhornia Crassipes)		Langmuir	Pseudo-second Order	Murithi, et al., 2014.

Table 4.2: Continued.

Biosorbents	**Types of Biosorbents**	**Isotherm Study**	**Kinetic Study**	**References**
Cynodon Dactylon	Agricultural Waste	Langmuir and Freundlich	-	Jha and Kumari, 2020.
Tea Waste		Langmuir and Freundlich	Pseudo-second Order	Ghasemi, Mafi Gholami and Yazdanian, 2016.
Residue of Padina Gymnospora Waste	Algae	Temkin	Pseudo-second Order	Mohamed, et al., 2019.
Ulva Fasciata		Langmuir	Pseudo-second Order	Nessim, et al., 2011.
Immobilized Microcystis Aeruginosa	Bacteria	Freundlich and Temkin	Pseudo-second Order	Wang, et al., 2014.
Recombinant Escherichia Coli with 33wt% Biomass		Langmuir	Pseudo-second Order	Kao, et al., 2009.
Aspergillus Niger	Fungi	Langmuir	-	Munawar, et al., 2018.

Table 4.2: Continued.

Biosorbents	Types of Biosorbents	Isotherm Study	Kinetic Study	References
Bamboo Charcoal	Activated Carbon	Langmuir	Pseudo-second Order	Wang, Wang and Ma, 2009.
Biochars from Eichornia Crassipes		Langmuir	Pseudo-second Order	Li, et al., 2016.
Surface-modified Activated Carbon		Langmuir	Pseudo-second Order	Liang, Liu and Zhang, 2016.
Pinus Halepensis Sawdust		Freundlich	Pseudo-second Order	Semerjian, 2010.

Table 4.2 shows that most of the biosorbents are best expressed using Langmuir isotherm as well as the pseudo-second order kinetic model. This indicates that the cadmium biosorption happens at specific adsorption site of biosorbent surface only and saturation is reached once the sites are fully occupied as illustrated in Figure 4.1. Besides, the homogeneous binding of cadmium ions onto the adsorption sites is not affected by the neighbouring adsorbed cadmium ions as they do not interact with each other (Czepirski, Balys and Komorowska- Czepirska, 2000).

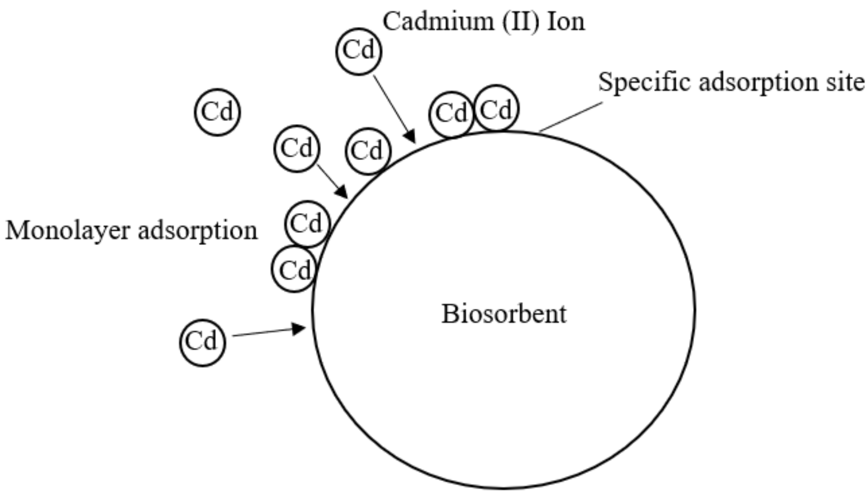

Figure 4.1: Langmuir Model Adsorption Mechanism.

On top of that, the study proves that most of the biosorbents fit pseudo-second order kinetic model indicates that the cadmium biosorption processes were limited by chemisorption, complexation, chelation or coordination and diffusion as reported by Febrianto, et al. (2008).

4.2 Effect of Operating Parameters on Cadmium Biosorption

Based on the past researches, batch adsorption experiments were normally conducted at different operating conditions to evaluate their effects on cadmium biosorption for different biosorbents. The optimum operating conditions usually provides the best biosorption performance for that particular biosorbent. In this parameter study, agricultural waste is selected to be studied due to their promising biosorption efficiency as discussed in Section 4.1.3.

4.2.1 Effect of pH on Biosorption Performance

Cadmium solution pH is the most significant parameter which greatly influences the biosorption performance. This is because the surface charges of the biosorbents are influenced by the changes in the solution pH (Saikaew and Kaewsarn, 2009). pH values which is too low or too high are not suitable for adsorption to take place. The effect of solution pH on the cadmium biosorption utilizing five different biosorbents such as dragonfruit peel, sweet potato peel, coffee ground, unmodified rice straw and mango peel, is shown in Figure 4.2 (Tanasal, La-Nafie and Taba, 2015; Asuquo and Martin, 2016; Azouaou, et al., 2010; Ding, et al., 2012; Iqbal, Saeed and Zafar, 2009).

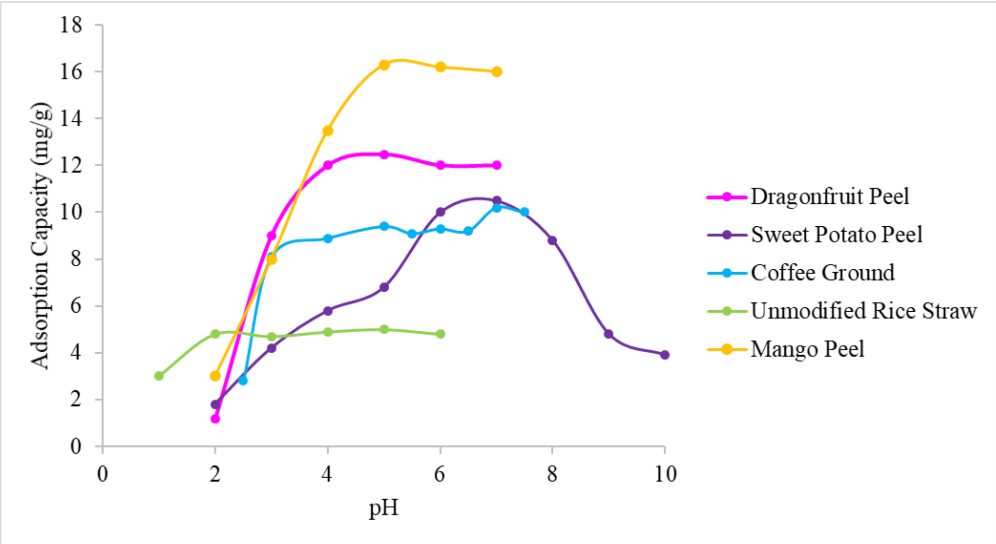

Figure 4.2: Effect of pH on Adsorption Uptake of Cadmium by Different Biosorbents (Tanasal, La-Nafie and Taba, 2015; Asuquo and Martin, 2016; Azouaou, et al., 2010; Ding, et al., 2012; Iqbal, Saeed and Zafar, 2009).

Figure 4.2 suggests that the biosorption uptake of cadmium by different biosorbents increases gradually when the pH value is increased from acidic to neutral, until an optimum adsorption uptake is achieved at pH of 5−7. This trend is well observed for all the biosorbents (Tanasal, La-Nafie and Taba, 2015; Asuquo and Martin, 2016; Azouaou, et al., 2010; Ding, et al., 2012; Iqbal, Saeed and Zafar, 2009). Furthermore, a further increase in solution pH from 7 to 10 in the work of Asuquo and Martin (2016) which used sweet potato peel was found to decrease the cadmium biosorption uptake from 10.5 mg/g to 4 mg/g. From the Figure 4.2, the optimum pH values for biosorption of cadmium from aqueous solution by mango peel, dragonfruit peel and unmodified rice straw is pH 5 with the adsorption uptake of 16 mg/g, 12 mg/g and 5 mg/g, respectively, whereas, coffee ground and sweet potato peel show the optimum adsorption uptake of cadmium at pH 7 which are around 8 mg/g and 10 mg/g respectively. This indicates that the cadmium biosorption is preferrable to take place in slight acidic and neutral environment.

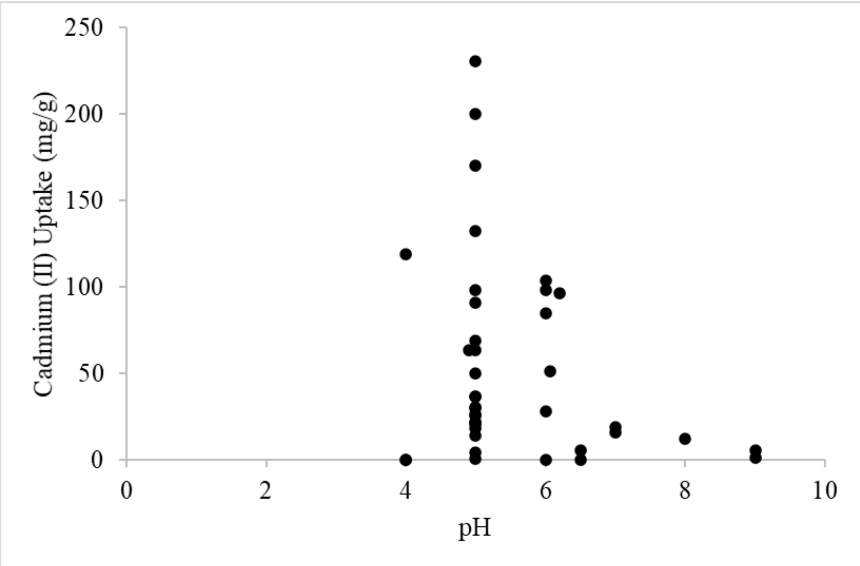

Figure 4.3: Optimum pH on Cadmium (II) Uptake by Different Biosorbents.

The optimum pH range of 5−7 that is suggested by Figure 4.2 is further strengthen by the summary on the optimum pH for maximum cadmium biosorption, as shown in Figure 4.3, which is plotted based on the results in Table 4.1. The figure concludes that most of the biosorbents can provide a high and promising biosorption efficiency at pH 5 and pH 6. The slight acidic-neutral environment is more conducive for cadmium biosorption than alkaline condition. This is mainly related to the pH point of zero charge (pH_{PZC}) of the biosorbents which are normally reported in a range of 4−7 (Iqbal, Saeed and Zafar, 2009; Lakshmipathy, Vinod and Sarada, 2013; Asuquo and Martin, 2016). The surface charge of biosorbent turns negative once the solution pH is higher than pH_{PZC}, hence the positive charged cadmium ions are able to adsorb onto the biosorbent due to the strong electrostatic attraction (Iqbal, Saeed and Zafar, 2009). In contrast, when the solution pH is below the pH_{PZC} of the biosorbents, repulsive force exists between the cadmium ions and positively charged biosorbent surface, which leads to low biosorption.

Moreover, there are high concentration of free hydrogen ions in extremely low pH metal solution. The hydrogen ions will compete the binding sites of biosorbents with positively charged cadmium ions, which further result in low cadmium adsorption uptake. The concentration of free hydrogen ions decreases ss the solution pH increases, which results in the decrease of competitive adsorption. Thus, higher cadmium biosorption performance is observed. Nevertheless, it is noteworthy that once the solution pH is higher than the optimum pH, cadmium precipitation begins to take place due to the existence of hydroxide ions in the solution, which further decrease the biosorption uptake (Iqbal, Saeed and Zafar, 2009; Ding, et al., 2012).

4.2.2 Effect of Solution to Biosorbent Dosage Ratio on Biosorption Performance

The performance of biosorbents is also highly affected by the biosorbent dosage as different mass of biosorbent provides different amount of binding sites. Since the volume of cadmium solution will also influence the effect of biosorbent dosage, hence the effect of solution to biosorbent dosage ratio is evaluated. The effect of solution to biosorbent dosage ratio on cadmium biosorption using five different biosorbents such as watermelon rind, coffee ground, mango peel, tea waste and unmodified rice straw is illustrated in Figure 4.4 (Lakshmipathy, Vinod and Sarada, 2013; Azouaou, et al., 2010; Iqbal, Saeed and Zafar, 2009; Ghasemi, Mafi Gholami and Yazdanian, 2016; Ding, et al., 2012).

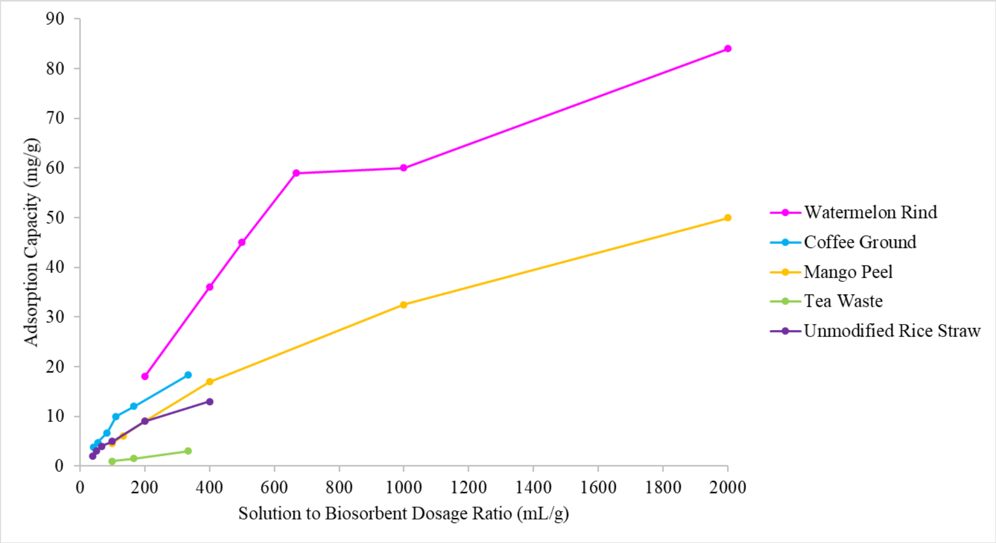

Figure 4.4: Effect of Solution to Biosorbent Ratio on Adsorption Uptake of Cadmium by Different Biosorbents (Lakshmipathy, Vinod and Sarada, 2013; Azouaou, et al., 2010; Iqbal, Saeed and Zafar, 2009; Ghasemi, Mafi Gholami and Yazdanian, 2016; Ding, et al., 2012).

Figure 4.4 illustrates an increasing trend for cadmium biosorption uptake, when the solution to biosorbent dosage ratio is increased, regardless of the types of biosorbents. A higher ratio suggests that the biosorbent dosage is low. At this condition, the cadmium uptake per unit biosorbent is higher as there are abundance of cadmium ions to compete for limited number of free adsorption site. All the free-exposed binding sites of biosorbent can be fully utilized by the available mobile cadmium ions, hence higher adsorption uptake can be achieved. In contrast, at lower solution to biosorbent dosage ratio, the biosorbent dosage is relatively higher than the amount of cadmium ions available in the solution. Therefore, this will result in the incomplete distribution of cadmium ions onto the binding sites of the biosorbent and hence decrease in the cadmium uptake.

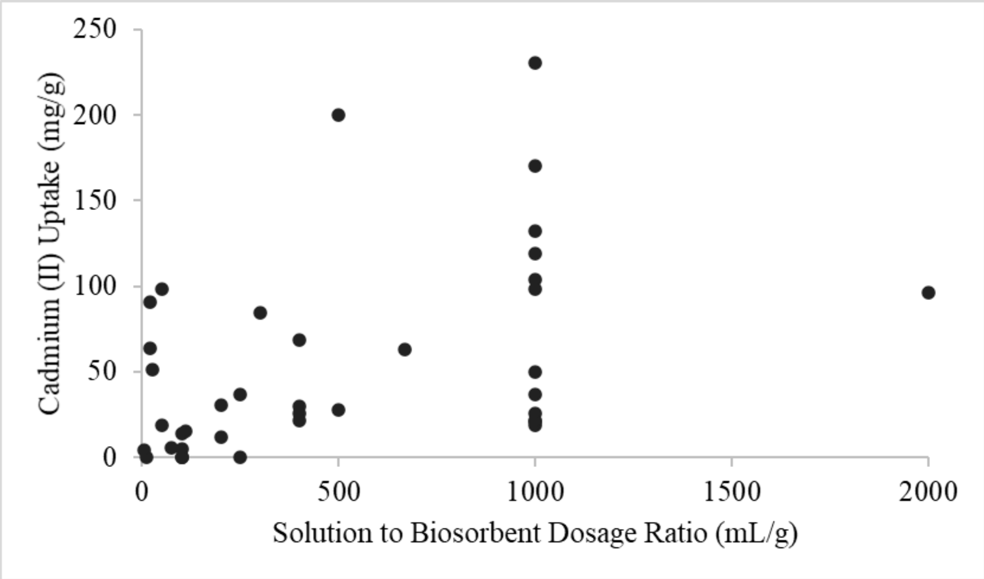

Figure 4.5: Optimum Solution to Biosorbent Dosage Ratio on Cadmium (II) Uptake by Different Biosorbents.

Figure 4.5 shows a summary on the reported optimum solution to biosorbent dosage ratio on cadmium uptake, which are plotted based on Table 4.1. The figure shows that most of the biosorbents have the optimum solution to biosorbent dosage ratio at ≤1000 mL/g for maximum biosorption performance.

4.2.3 Effect of Contact Time on Biosorption Performance

Contact time for biosorption is another significant parameter that influence biosorption of cadmium. The effect of contact time on cadmium biosorption utilizing five different biosorbents such as dragonfruit peel, sweet potato peel, mango peel, tea waste and coffee ground is depicted in Figure 4.6 (Tanasal, La-Nafie and Taba, 2015; Asuquo and Martin, 2016; Iqbal, Saeed and Zafar, 2009; Ghasemi, Mafi Gholami and Yazdanian, 2016; Azouaou, et al., 2010).

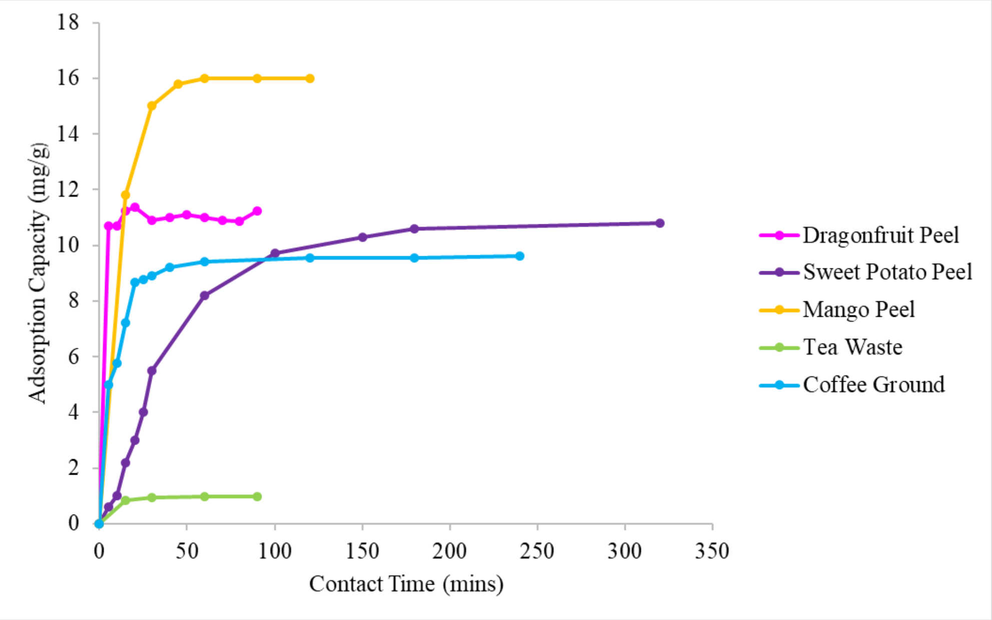

Figure 4.6: Effect of Contact Time on Adsorption Uptake of Cadmium by Different Biosorbents (Tanasal, La-Nafie and Taba, 2015; Asuquo and Martin, 2016; Iqbal, Saeed and Zafar, 2009; Ghasemi, Mafi Gholami and Yazdanian, 2016; Azouaou, et al., 2010).

Figure 4.6 illustrates that the cadmium uptake is increasing with the contact time between the solution and biosorbents and the equilibrium uptake is observed after prolonged contact time, regardless of the types of biosorbents. At the initial stage of biosorption, there are many free-exposed sites for binding on the biosorbent surface to interact with the mobile cadmium (II) ions in aqueous solution. Therefore, the adsorption uptake rises rapidly as the cadmium ions bind onto the binding sites. However, the biosorption rate becomes slower as the contact time increases, as a result of that the sites for binding are almost occupied with the cadmium ions. Once all the binding sites are fully occupied or saturated with the cadmium ions, cadmium biosorption achieves equilibrium.

Nevertheless, it is worth noting that the optimum contact time is highly dependent on the types of biosorbents. Based on Figure 4.6, the optimum contact time is in the order of dragonfruit peels (20-30 minutes) < tea waste (30 minutes) < mango peels (60 minutes) < sweet potato peel (120 minutes) < coffee ground (180 minutes).

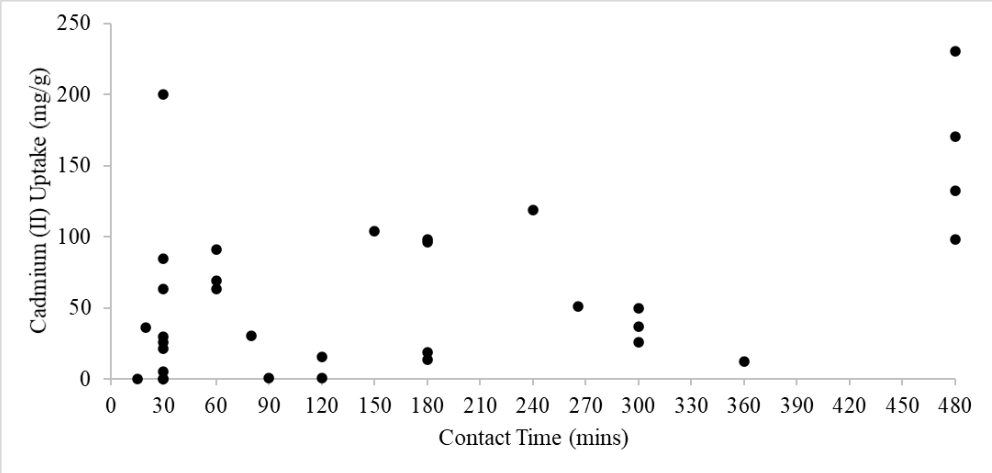

Figure 4.7: Optimum Contact Time in Minutes on Cadmium (II) Uptake by Different Biosorbents.

A summary on the optimum contact time for cadmium biosorption is shown in Figure 4.7, which are reported by researchers as shown in Table 4.1. From the figure, it can be concluded that the cadmium biosorption can achieve equilibrium within three hours (equivalent to 180 minutes). To be more precise, 69.7 % of studies reported that the equilibrium can be achieved within three hours of contact time between the cadmium solution and the biosorbents.

4.3 Biosorbent Surface Area Characterisation

The surface morphology of biosorbents involved in removing cadmium ions from water can be analysed and observed through Brunauer-Emmett-Teller (BET) and Scanning Electron Microscopy (SEM). According to Asuquo and Martin (2016), the sweet potato peel has rough crevices as observed through SEM analysis. Moreover, the SEM analysis of orange peel, litchi peel, pomegranate peel and banana peel also showed the presence of rough, loose, microporous surface on the biosorbents as reported by Chen, et al. (2018). An irregular and rough surface of sesame provides a large contact area between the biosorbent and cadmium as observed by Cheraghi, Ameri and Moheb (2015). Therefore, the biosorbents are normally have rough surface for providing large surface area to the adsorbate.

On top of that, BET analysis was also carried out by the researchers to discover the pore size and the surface area of biosorbents. For instance, Asuquo and Martin (2016) reported that the surface area was 1.91 m^2 per 1g of sweet potato peel. The result as stated by Ghasemi, Mafi Gholami and Yazdanian (2016) showed that the surface area was 0.79 m^2 per 1g of tea waste. This is due to the nature of lignin, hemicellulose and cellulose content present in the lignocellulosic biosorbents, hence they are known to have low surface area as well as wide distributions of pore size. These wide distributions of pore size in the lignocellulosic materials may facilitate the diffusion of cadmium ions from solution into biosorbent (Asuquo and Martin, 2016). Since the surface area of tea waste is smaller than the sweet potato peel, so it has a lower adsorption uptake which is only 0.497 mg/g as compared to sweet potato peel (18.8 mg/g) as tabulated in Table 4.1.

4.4 Removal Mechanism for Cadmium Biosorption

Cadmium biosorption takes place on account of the interaction among the positively charged of cadmium ions and the negatively charged biosorbent surface. In fact, there are several removal mechanisms occur simultaneously to result in the cadmium biosorption, which is mainly determined through Fourier Transform Infrared Spectroscopy (FTIR) and Energy Dispersive X-ray (EDX) analysis.

According to Asuquo and Martin (2016), the mechanism of metal ion sorption can be proven through the identification of adsorbed metal ions on biosorbent after the biosorption process through EDX analysis. This is also supported by Lakshmipathy, Vinod and Sarada (2013), where the ion exchange mechanism was stated to be involved in the cadmium removal by watermelon rind due to the difference in the chemical composition of positively charged ions such as potassium and magnesium on biosorbent was observed before and after the biosorption process. This indicates that the positively charged ions are replaced by cadmium ions through the ion exchange mechanism.

It is also significant to ascertain the functional groups that are available on the biosorbents due to their significant impact and important role on the removal mechanism for cadmium biosorption. This is because the presence of certain active groups on the biosorbent can interact with the cadmium ions through bonding formation, complexation or electrostatic interactions to carry away the ions from the solution. Functional groups of biosorbents can be determined using FTIR analysis where the interaction between the biosorbents and cadmium ions can be observed through the shifting of wavenumber due to the changes in coordination sites.

Carboxyl and hydroxyl groups are the most abundant and predominant functional groups that are responsible in removing the cadmium from aqueous solution as reported by most of the researchers. The interaction usually takes place between the carboxylate and hydroxylate anions with cadmium ions (Lakshmipathy, Vinod and Sarada, 2013; Azouaou, et al., 2010; Iqbal, Saeed and Zafar, 2009). It was usually observed that C-H stretching of methylene and methyl groups in hemicellulose, cellulose and lignin on the biosorbents. Furthermore, C=C stretching as well as C=O stretching of ionic or esterified carboxylic groups are also found and this indicate the presence of aromatic compounds in lignin of the biosorbents (Asuquo and Martin, 2016). The presence of C-O groups of ether, phenolic, alcoholic, ester and carboxylic acid on biosorbent can also be observed as stated by Chen, et al. (2018).

In addition, hydroxyl (-OH) group is mainly contributing to the covalent coordination bonding with cadmium ions (Tanasal, La-Nafie and Taba, 2015). The presence of alcoholic, phenolic and carboxylic acids (-COOH) compounds by steric effects in the hemicellulose, cellulose, lignin and pectins of the biosorbent contain the hydroxyl group (Chen, et al., 2018; Tanasal, La-Nafie and Taba, 2015; Cheraghi, Ameri and Moheb, 2015; Asuquo and Martin, 2016). Cadmium ions will combine with the molecules which contain free electron pairs to form a complex through the covalent coordination bonding.

Moreover, cadmium ions can also be removed in the presence of amino group (-NH). According to Saikaew and Kaewsarn (2009), Gillbert, et al. (2011) and Sanusi, Umar and Abdullahi (2015), the chemical interactions between the amino groups and cadmium ions was observed to be taken place on the biosorbent surface.

In short, the cadmium ions can be removed in the presence of abundant oxygenated surface group such as acidic, hydroxyl and carboxyl groups as well as the amino group which are found in the cellulose, hemicellulose, lignin and pectins of biosorbents. The chemical interaction which takes place between the functional groups of biosorbents and cadmium ions through the removal mechanism such as surface adsorption, chelation and complexation is shown in Figure 4.8.

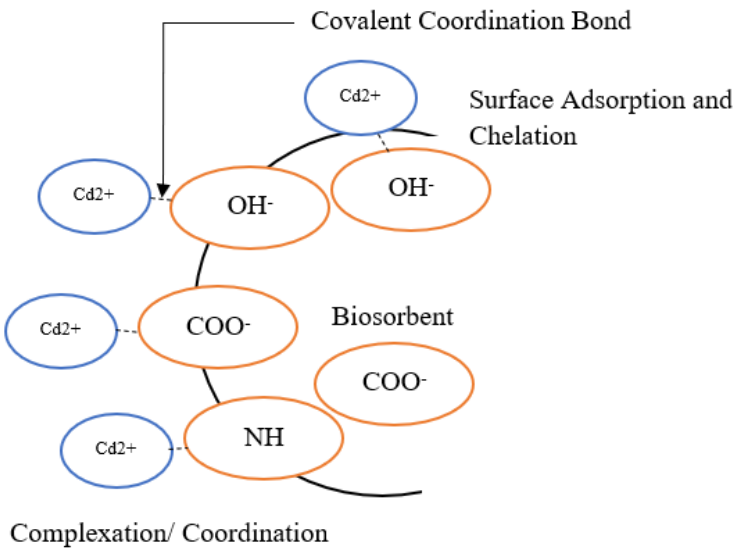

Figure 4.8: Removal Mechanism by Functional Groups of Biosorbent.

4.5 Evaluation of Avocado Peel as Biosorbent in Cadmium Removal

Avocado peel is selected as the biosorbent to investigate for its suitability in this study due to its simple structure and availability throughout the year. Besides, it is considered as novel biosorbent candidate because there is no research study on the removal of cadmium ion by using avocado peel.

Avocado peel is easily available due to its increasing market demand. According to Mordor Intelligence (2019), the globally avocado consumption in 2018 was USD 9.29 billion with 5.03% Compound Annual Growth Rate (CAGR). For instance, China market demand for avocado increases which they imported 22% more avocado in 2017 than previous year. In Malaysia, there is also an increasing trend of avocado fruit market and it is expected to increase in future (Index Box, 2020). Therefore, the generation of avocado waste residues especially avocado peel is increasing as well.

Avocado, which is also known as *Persea americana* is usually comes from Meixco and Central America (Hurtado-Fernández, Fernández-Gutiérrez and Carrasco-Pancorbo, 2018). It has a pear-like shaped, sometimes it is in oval or nearly round appearance. The avocado peels may be appeared in yellow-green, dark green, reddish purple, or dark purple colour with tiny yellow dots. The peels could have smooth or dull surface, different skin thickness and skin peel ability (Araújo, et al., 2018). Avocado fruit usually consists of edible fruit pulp (mesocarp), a seed covered with endocarp, and avocado peel (exocarp) as shown in Figure 4.9. Figure 4.10 illustrates the avocado peels which are ready to be implemented as biosorbent.

Figure 4.9: Avocado Fruit (Hurtado-Fernández, Fernández-Gutiérrez and Carrasco-Pancorbo, 2018).

Figure 4.10: Avocado Peel (Butterfield, 2013).

Avocado is well known with its nutritional content and benefits to human health, hence it is widely available in the market nowadays. Avocado pulp contains high amount of insoluble and soluble fibres, proteins and sugars as compared to other fruits (Araújo, et al., 2018). Avocado pulp is usually being utilised to derive different kind of products. For instance, avocado fruit can be sold as fresh fruit or processed into different products such as avocado oil and sauces. Avocado oil is applicable for manufacturing of food and cosmetic products. However, the peel and seed of avocado fruit has no commercial usage and normally being managed as waste (Domínguez, et al., 2014).

According to Jimenez, et al. (2020), both avocado pulp and waste contain bioactive compounds which can aid in various biological activities such as antimicrobial, antifungal, antioxidant and lipid and protein oxidation inhibition (Araújo, et al., 2018). Avocado peels also contain around 0.75 to 1.6% ash, 2.89 to 11.04% total lipids, 1.51 to 6.3% protein, 20.8% nitrogen-free extract, 6.85 to 56.9% fiber and 65.7 to 76.9% moisture (Jimenez, et al., 2020).

4.5.1 Functional Groups of Avocado Peels

The functional groups that are present on avocado peel have to be determined to enhance the cadmium biosorption as the removal mechanism is greatly influenced by the functional groups. Since avocado peel is novel biosorbent, only two literatures were found for reporting the surface functional groups of avocado peels (Pawar, Theodore and Hiremath, 2019; Mallampati, et al., 2015).

Avocado peel was treated chemically by Pawar, Theodore and Hiremath (2019) to synthesize the hydroxyapatite nanoparticles to conduct the chromium (VI) biosorption. It was observed through XRD analysis that the existence of hydroxyapatite particles on the chemically treated avocado peel which can help in the removal of metal ion due to their crystallize structure. The functional groups include carbonate group and hydroxyl group were discovered on the hydroxyapatite nanoparticles which are responsible in attracting and removing the positively charged metal ions.

In addition, work of Mallampati, et al. (2015) showed the functional groups of hydroxyl and carboxyl on avocado peel were available in removing the nickel ions from water. The -OH, C=O and C=C stretching, angular deformation in C-H bonds as well as axial C-O bonds were observed from the FTIR analysis. This is mainly due to the presence of esters, carboxylic acid, aromatic rings and phenols on avocado peel. This is supported by Araújo, et al. (2018) who stated that avocado peel contains high amount of fibres, proteins and sugars which contributes to abundant hydroxyl and carboxyl groups.

As discussed in Section 4.4, cadmium (II) ions are normally removed in the presence of acidic, carboxyl and hydroxyl groups. Therefore, avocado peel which contains these carboxyl and hydroxyl group is expected to have significant efficiency in removing the cadmium ions.

4.5.2 Important Operating Parameters for Cadmium Biosorption using Avocado Peel

In this study, it is suggested to treat cadmium contamination using the avocado peel in the paper mill industry wastewater, Taloja Industrial Estate, Mumbai with 20-27.5 mg/L initial cadmium concentration (Lokhande, Singare and Pimple, 2011). Few characterizations of the effluents of paper mill industry wastewater are summarized in Table 4.3.

Table 4.3: Characteristics of Paper Mill Industry Wastewater Effluents in Taloja Industrial Area of Mumbai (Lokhande, Singare and Pimple, 2012).

Characteristics	Average Values
Temperature	32.1 ℃
pH	8.2
Biochemical Oxygen Demand	86.7 mg/L
Chemical Oxygen Demand	253.8 mg/L
Total Solids	3585.3 mg/L
Total Suspended Solids	517.7 mg/L
Total Dissolved Solids	3067.7 mg/L

Based on Section 4.5.1, there are sufficient functional groups which are the carboxyl and hydroxyl group found on avocado peel, thus it is expected to have similar removal mechanism as other biosorbents in cadmium biosorption. Therefore, the trend of operating parameters for cadmium biosorption using avocado peel is also expected to be similar as per discussed in Section 4.2. The predictions of optimum conditions are most likely to be at a range of pH 5−7, solution to biosorbent dosage ratio less than 1000 mL/g and contact time within three hours. The wastewater has a slightly alkaline condition as reported by Lokhande, Singare and Pimple (2012). Hence, the wastewater is not readily to be used and a pH adjustment is required to modify the pH of the solution, so that it is suitable for the cadmium biosorption by avocado peel.

The proposed operating conditions are also in line with the reported literatures on the biosorption of nickel using avocado peels. The work of Mallampati, et al. (2015) suggests that the optimum pH to remove nickel (II) ion is pH 4, which indicates that the biosorption process by avocado peel is preferrable to take place in slight acidic environment as discussed in Section 4.2.1. Also, according to Mallampati, et al. (2015), the hydroxyl and carboxyl groups present on avocado peel facilitate the cation biosorption at higher pH.

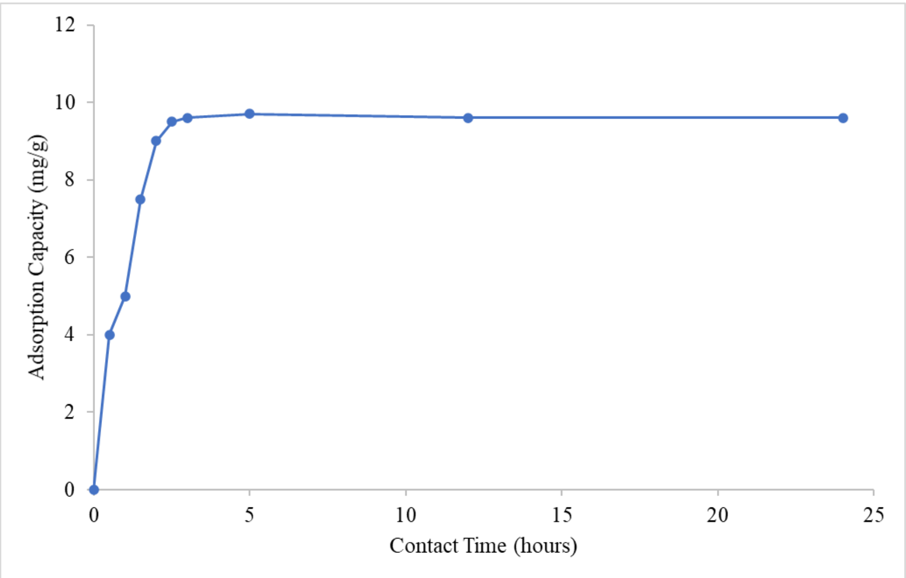

Figure 4.11: Effect of Contact Time on The Adsorption Uptake of Nickel (II) Ions by Avocado Peel (Mallampati, et al., 2015).

In contrast, the optimum contact time for nickel biosorption by avocado peel was reported to be three hours as shown in Figure 4.11 (Mallampati, et al., 2015), which was similar to the general optimum contact time by other biosorbents as discuss previously in Section 4.2.3.

Table 4.4: Avocado Peels as Biosorbent.

Solute Targeted	Operational Conditions	Metal Uptake (mg/g)	References
Ni^{2+}	pH: 4; Contact Time: 3 hours	9.82	Mallampati, et al., 2015.
Cr^{6+}	Contact Time: 30 mins	4.36	Pawar, Theodore and Hiremath, 2019.

Table 4.4 shows the optimum operating conditions that are reported for biosorption using avocado peels. It is observed that the metal uptake performance of avocado peel is ranged from 4 to 10 mg/g for different metal uptake at different operational conditions. This might be due to different metal ions have different affinity to be adsorbed on the biosorbent surface. The optimum pH of the solution is pH 4 (for divalent nickel cation) and the optimum contact time is ranged from 30 minutes up to three hours for the metal biosorption by avocado peel. This is in line with the suggestion that is predicted based on Section 4.2.

4.5.3 Suitability of Avocado Peel as Biosorbent

The feasibility of avocado peel for cadmium removal from water should also be considered based on various factors. These factors include the effluent characteristics, biomass characteristics and process characteristics. Effluent characteristics such as the solution pH which alters the ionization degree of biosorbent and affect the biosorption performance. The biomass characteristics, such as the availability and adsorption uptake of avocado peel are important characteristics to be considered. Capital and operating costs of avocado peel biosorbent are the process characteristics which take the economic aspects into consideration.

First of all, the capital cost of avocado peel is considered to be low. Although the fresh avocado fruit is sold at a higher price in the market as compared to other imported fruits such as orange and apple, but the avocado peel can be easily obtained from the fruit sellers at a low price since it is considered as a waste. Also, due to its simplicity, the operating cost to pretreat the avocado peel and conducting the biosorption process is considered low as the batch experiment process is similar to other fruit waste biosorbent.

Besides, avocado peel is found to be highly available in Malaysia due to the increasing trend of avocado fruit market (Index Box, 2020). From Section 4.2, it can be concluded that most of the biosorbents perform the maximum cadmium uptake at slightly acidic to neutral environment and contact time within three hours which is similar to the nickel adsorption by avocado peel (Mallampati, et al., 2015), with solution to biosorbent dosage ratio of $\leq$1000 mL/g. The maximum divalent heavy metal uptake by avocado peel as shown in Table 4.4 was performed at a contact time of three hours and at pH 4, which is quite close to the parameters as discussed in Section 4.2.

Since avocado peel is still a novel biosorbent in cadmium biosorption, it is still difficult to conclude the exact cadmium uptake that will be expected. Nevertheless, the functional groups that available on the avocado peel surface are found to be hydroxyl and carboxyl groups, which are similar to the common biosorbents that are as discussed in Section 4.4. Due to the similar functional groups as other biosorbents, avocado peels are expected to be suitable to extract cadmium from water via biosorption.

Therefore, avocado peel is expected to have high efficiency in removing the cadmium ions from water after considering all the aspects. For instance, avocado peel is expected to be suitable to be applied to treat the cadmium contamination in the paper mill industry wastewater, Taloja Industrial Estate, Mumbai with 20-27.5 mg/L initial cadmium concentration (Lokhande, Singare and Pimple, 2011). However, pH adjustment may be required to treat the wastewater. Avocado fruit is also easily available in Mumbai, the metro city in India as reported by New Delhi Television Food (2019).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In conclusion, biosorption process is found to be efficient in removing the cadmium (II) ions from water. It is not only environmentally friendly, but also cost effective by utilising the potential biosorbents. There are different types of biosorbents such as bacteria, algae, fungi and agricultural waste. Among them, agricultural waste especially fruit waste is found to be the most promising biosorbent as it has high cadmium uptake as compared to other biosorbents (in which the cadmium uptake is: agricultural waste > algae > bacteria > activated carbon > fungi). The maximum cadmium uptake of 1000 mg/g was reported to achieve using defatted papaya seed at pH 5 with 100 mL/g of solution to biosorbent dosage ratio at 20 minutes contact time.

The biosorbents show different biosoption performance at different operating conditions. In general, biosorbents preferably to perform maximum cadmium biosorption in slightly acidic to neutral environment which is in the range of pH 5−7. It is also found that higher solution to biosorbent dosage ratio shows a better biosorption performance for all the biosorbens and the optimum ratio is usually at ≤1000 mL/g. The biosorption performance are observed to be increased linearly with the contact time and an equilibrium uptake will be achieved after prolonged contact time, in which the typical contact time is within three hours.

The biosorption of cadmium from water are reported to follow Langmuir isotherms and pseudo-second order kinetic models. This represents that the cadmium biosorption tends to occur as single layer adsorption on the biosorbent surface. The responsible functional groups in cadmium biosorption are acidic, amino, hydroxyl and carboxyl groups. Chemical interaction could take place between these functional groups and cadmium ions through the removal mechanism such as surface adsorption and complexation, chelation or coordination and diffusion.

In this study, it is also suggested that avocado peel as novel biosorbent is suitable for the cadmium removal in industrial wastewater. This is because avocado peel is highly available in the world and the biosorbents can be prepared easily. Besides, the hydroxyl and carboxyl groups are available on the avocado peel, which are responsible in the biosorption of cadmium. Based on the analysis from the literature, it is predicted that the biosorption process on avocado peels will happen at a condition of pH = $4-7$, solution to biosorbent dosage ratio at $\leq$1000 mL/g and contact time within three hours.

5.2 Recommendations for Future Work

Since the potential of avocado peel as biosorbent in removal of cadmium from water is not proven experimentally, thus a future study on cadmium biosorption utilizing avocado peel can be conducted experimentally. There are two recommendations provided as below to consolidate the suitability of avocado peel as biosorbent as well as to provide a better insight in future research:

(i) Physical and chemical surface modification can be conducted to improve the surface area of avocado peel to enhance the cadmium adsorption onto the binding sites.

(ii) Biosorption study can be performed in both continuous and batch mode to analyse the biosorption performance as the simulation of biosorption environment in real plant.

REFERENCES

Ahalya, N., Ramachandra, T. V., and Kanamadi, R. D., 2003. Biosorption of heavy metals. *Research Journal of Chemistry and Environment*, 7(4), pp. 1–13.

Ahn, C. K., Park, D., Woo, S. H. and Park, J. M., 2008. Removal of cationic heavy metal from aqueous solution by activated carbon impregnated with anionic surfactants. *Journal of hazardous materials*, 164(2009), pp. 1130–1136.

Al-Jlil, S. A., 2010. Removal of heavy metals from industrial wastewater by adsorption using local bentonite clay and roasted date pits in Saudi Arabia. *Trends in Applied Sciences Research*, 5(2), pp. 138–145.

Araújo, R. G., Rodriguez-Jasso, R. M., Ruiz, H. A., Pintado, M. M. E. and Aguilar, C. N., 2018. Avocado by-products: Nutritional and functional properties. *Trends in Food Science & Technology,* 80, pp. 51–60.

Asuquo, E. D. and Martin, A. D., 2016. Sorption of cadmium (II) ion from aqueous solution onto sweet potato (Ipomoea batatas L.) peel adsorbent: Characterisation, kinetic and isotherm studies. *Journal of Environmental Chemical Engineering*, 4(4), pp. 4207–4228.

Ayawei, N., Ebelegi, A. N. and Wankasi, D., 2017. Modelling and interpretation of adsorption isotherms. *Journal of Chemistry*, 2017, pp. 1–11.

Azimi, A., Azari, A., Rezakazemi, M. and Ansarpour, M., 2017. Removal of heavy metals from industrial wastewaters: A review. *ChemBioEng Reviews*, 4(1), pp. 37–59.

Azouaou, N., Sadaoui, Z., Djaafri, A. and Mokaddem, H., 2010. Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics. *Journal of hazardous materials,* 184(1-3), pp. 126–134.

Beltrán-Hernández, R. I., Vázquez-Rodríguez, G. A., Juárez-Santillán, L. F., Martínez-Ugalde, I., Coronel-Olivares, C. and Lucho-Constantino, C. A., 2015. Cadmium removal from aqueous systems using Opuntia albicarpa L. Scheinvar as biosorbent. *BioMed research international*, 2015, pp.1–6.

Beni, A. A. and Esmaeili, A., 2019. Biosorption, an efficient method for removing heavy metals from industrial effluents: A review. *Environmental Technology & Innovation*, 17(2020), pp. 1–43.

Bloomfield, F., 2017. *Cadmium — toxicity, side effects, diseases and environmental impacts.* [online] Available at: < https://naturalpedia.com/cadmium-toxicity-side-effects-diseases-and-environmental-impacts.html> [Accessed 28 June 2020].

Butterfield, M., 2013. *How to freeze avocados.* [online] Available at: <http://www.onehundreddollarsamonth.com/how-to-freeze-avocados/> [Accessed 8 August 2020].

Chen, C. and Wang, J. L., 2009. Biosorbents. In: Y. Liu, and J. L. Wang, eds. 2009. *Fundamentals and applications of biosorption isotherms, kinetics and thermodynamics*. New York, United States: Nova Science Publishers, pp. 29–80.

Chen, C. and Wang, J. L., 2009. Factors influencing biosorption process. In: Y. Liu, and J. L. Wang, eds. 2009. *Fundamentals and applications of biosorption isotherms, kinetics and thermodynamics*. New York, United States: Nova Science Publishers, pp. 213–230.

Chen, C. and Wang, J. L., 2009. General mechanisms of biosorption. In: Y. Liu, and J. L. Wang, eds. 2009. *Fundamentals and applications of biosorption isotherms, kinetics and thermodynamics*. New York, United States: Nova Science Publishers, pp. 155–212.

Chen, Y., Wang, H., Zhao, W. and Huang, S., 2018. Four different kinds of peels as adsorbents for the removal of Cd (II) from aqueous solution: Kinetics, isotherm and mechanism. *Journal of the Taiwan Institute of Chemical Engineers*, 88, pp. 146–151.

Cheraghi, E., Ameri, E. and Moheb, A., 2015. Adsorption of cadmium ions from aqueous solutions using sesame as a low-cost biosorbent: Kinetics and equilibrium studies. *International Journal of Environmental Science and Technology*, 12(8), pp. 2579–2592.

Chintalpudi, V. K., ed., 2018. *Biosorption.* Rijeka: IntechOpen.

Connor, N., 2020. *Cadmium – discoverer – year of discovery.* [online] Available at: <https://www.periodic-table.org/Cadmium-discoverer/> [Accessed 30 June 2020].

Connor, N., 2020. *Thermal properties of cadmium – Cd.* [online] Available at: <https://www.periodic-table.org/cadmium-thermal-properties/> [Accessed 30 June 2020].

Crini, G. and Lichtfouse, E., 2018. Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters*, 17(1), pp. 145–155.

Czepirski, L., Balys, M. R. and Komorowska-Czepirska, E., 2000. Some generalization of Langmuir adsorption isotherm. *Internet Journal of Chemistry*, 3(14), pp. 1–27.

Department of Environment Malaysia, 2009. *Environmental Quality (Industrial Effluent) Regulations, 2009. Environmental Quality Act 1974 (Act 127) & Subsidiary Legislation.* Kuala Lumpur: Percetakan Nasional Malaysia Berhad.

Derek, 2017. *How is reverse osmosis different from filtration.* [online] Available at: <https://www.best-ro-system.com/difference-from-filtration/> [Accessed 11 July 2020].

Ding, Y., Jing, D., Gong, H., Zhou, L. and Yang, X., 2012. Biosorption of aquatic cadmium (II) by unmodified rice straw. *Bioresource technology*, 114, pp. 20–25.

Domínguez, M. P., Araus, K., Bonert, P., Sánchez, F., San Miguel, G. and Toledo, M., 2016. The avocado and its waste: An approach of fuel potential/application. In: G. Lefebvre, E. Jiménez, and B. Cabañas, eds. 2016. *Environment, energy and climate change II*. Cham: Springer International Publishing, pp. 199–223.

Duruibe, J. O., Ogwuegbu, M. O. C., Egwurugwu, J. N., 2007. Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*, 2(5), pp. 112–118.

Farhan, A. M., Al-Dujaili, A. H. and Awwad, A.M., 2013. Equilibrium and kinetic studies of cadmium (II) and lead (II) ions biosorption onto ficus carcia leaves. *International Journal of Industrial Chemistry*, 4(24), pp. 1–8.

Fawzy, M., Nasr, M., Helmi, S. and Nagy, H., 2016. Experimental and theoretical approaches for Cd (II) biosorption from aqueous solution using Oryza sativa biomass. *International journal of phytoremediation*, 18(11), pp. 1096–1103.

Febrianto, J., Kosasih, A. N., Sunarso, J., Ju, Y.-H., Indraswati, N. and Ismadji, S., 2008. Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. *Journal of hazardous materials*, 162(2009), pp. 616–645.

Gautam, R. K., Chattopadhyaya, M. C. and Sharm a, S. K., 2013. Biosorption of heavy metals: Recent trends and challenges. In: S. K. Sharma, and R. Sanghi, eds. 2013. *Wastewater reuse and management*. Dordrecht: Springer Netherlands, pp. 305–322.

Gautam, R. K., Mudhoo, A., Lofrano, G. and Chattopadhyaya, M. C., 2014. Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration. *Journal of Environmental Chemical Engineering*, 2(1), pp. 239–259.

Gautam, R. K., Sharma, S. K., Mahiya, S. and Chattopadhyaya, M. C., 2014. Contamination of heavy metals in aquatic media: Transport, toxicity and technologies for remediation. In: S. Sharma, ed. 2014. *Heavy metals in water*. Cambridge: Royal Society of Chemistry, pp. 1–24.

Ghasemi, S., Mafi Gholami, R. and Yazdanian, M., 2016. Biosorption of heavy metal from cadmium rich aqueous solutions by tea waste as a low cost bio-adsorbent. *Jundishapur Journal of Health Sciences*, 9(1), pp. 1–8.

Gilbert, A. U., Emmanuel, U. I., Adebanjo, A. A. and Olalere, A. G., 2011. Biosorptive removal of Pb2+and Cd2+ onto novel biosorbent: Defatted Carica papaya seeds. *Biomass and Bioenergy*, 35(7), pp. 2517–2525.

Goksungur Y., Uren S. and Guvenc U., 2005. Biosorption of cadmium and lead ions by ethanol treated waste baker's yeast biomass. *Bioresour Technol*, 96(2005), pp. 103–109.

Gunatilake, S. K., 2015. Methods of removing heavy metals from industrial wastewater. *Methods*, 1(1), pp. 12–18.

Hassan, S. R., Zwaina, H. M., Zamana, N. Q. and Dahlan, I., 2014. Recycled paper mill effluent treatment in a modified anaerobic baffled reactor: Start-up and steady-state performance. *Environmental technology*, 35(1-4), pp. 294–299.

Higson, D., 2017. *How does reverse osmosis work*. [online] Available at: <https://www.advancedwaterinc.com/how-reverse-osmosis-works/> [Accessed 9 July 2020].

Holan, Z. R., Volesky, B. and Prasetyo, I., 1993. Biosorption of cadmium by biomass of marine algae. *Biotechnology and Bioengineering,* 41, pp. 819–825.

Huang, Q., Hu, D., Chen, M., Bao, C. and Jin, X., 2019. Sequential removal of aniline and heavy metal ions by jute fiber biosorbents: A practical design of modifying adsorbent with reactive adsorbate. *Journal of Molecular Liquids*, 285, pp. 288–298.

Huang, Y., Zhao, R., Liu, W., Li, Y., Zhang, P., Wang, S. and Wang, L., 2018. Using pretreated chestnut endothelium to adsorb lead and cadmium ions from water. *Saudi journal of biological sciences*, 25(6), pp. 1154–1162.

Hurtado-Fernández, E., Fernández-Gutiérrez, A. and Carrasco-Pancorbo, A., 2018. Avocado fruit— Persea americana. In: S. Rodrigues, E. Oliveira Silva, and E. S. Brito, eds. 2018. *Exotic fruits*. Elsevier, pp. 37–48.

Idrees, N., Tabassum, B., Abd Allah, E. F., Hashem, A., Sarah, R. and Hashim, M., 2018. Groundwater contamination with cadmium concentrations in some West U.P. Regions, India. *Saudi journal of biological sciences*, 25(7), pp. 1365–1368.

Igunnu, E. T. and Chen, G. Z., 2012. Produced water treatment technologies. *International Journal of Low-Carbon Technologies*, 9(3), pp. 157–177.

Index Box, 2020. *Avocados - Malaysia - Report.* [online] Available at: <https://app.indexbox.io/report/080440/458/> [Accessed 10 August 2020].

Interstate Technology & Regulatory Council, 2010. *Chemical precipitation.* [online] Available at: <https://www.itrcweb.org/miningwaste-guidance/to_chem_precip.pdf> [Accessed 9 July 2020].

Iqbal, M., Saeed, A. and Zafar, S. I., 2009. FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd(2+) and Pb(2+) removal by mango peel waste. *Journal of hazardous materials*, 164(1), pp. 161–171.

Jha, A. K. and Kumari, K., 2020. Cadmium (II) removal by Cynodon dactylon and orange peel powder from aqueous medium by adsorption. *Science Academique*, 1(1), pp. 1–10.

Jiang, L., Tu, Y., Li, X. and Li, H., 2018. Application of reverse osmosis in purifying drinking water. *E3S Web of Conferences*, 38(01037), pp. 1–6.

Jimenez, P., Garcia, P., Quitral, V., Vasquez, K., Parra-Ruiz, C., Reyes-Farias, M., Garcia-Diaz, D. F., Robert, P., Encina, C. and Soto-Covasich, J., 2020. Pulp, leaf, peel and seed of avocado fruit: A review of bioactive compounds and healthy benefits. *Food Reviews International*, 70, pp. 1–37.

Kao, W.-C., Wu, J.-Y., Chang, C.-C. and Chang, J.-S., 2009. Cadmium biosorption by polyvinyl alcohol immobilized recombinant Escherichia coli. *Journal of hazardous materials*, 169(1–3), pp. 651–658.

Kaur, B., 2019. Penang baffled by claim of heavy-metal pollution off its northern coast. *New Straits Times.* [online] 5 Dec. Available at: <https://www.nst.com.my/news/nation/2019/05/487744/penang-baffled-claim-heavy-metal-pollution-its-northern-coast> [Accessed 29 June 2020].

Kongsricharoern, N., Polprasert, C., 1995. Electrochemical precipitation of chromium (Cr6+) from an electroplating wastewater. *Water Sci. Technol*, 31(9), pp. 109–117.

Kubier, A., Wilkin, R. T. and Pichler, T., 2019. Cadmium in soils and groundwater: A review. *Applied geochemistry: Journal of the International Association of Geochemistry and Cosmochemistry*, 108, pp. 1–16.

Kumar, P. S., Gayathri, R., Senthamarai, C., Priyadharshini, M., Fernando, P. S. A., Srinath, R. and Kumar, V. V., 2012. Kinetics, mechanism, isotherm and thermodynamic analysis of adsorption of cadmium ions by surface-modified Strychnos potatorum seeds. *Korean Journal of Chemical Engineering*, 29(12), pp. 1752–1760.

Lakshmipathy, R., Vinod, A. V. and Sarada, N. C., 2013. Watermelon rind as biosorbent for removal of Cd2+ from aqueous solution: FTIR, EDX, and kinetic studies. *J. Indian Chem. Soc.*, 90, pp. 1147–1154.

Lenntech, B. V., 2020. *Cadmium - Cd.* [online] Available at: <https://www.lenntech.com/periodic/elements/cd.htm> [Accessed 25 June 2020].

Lenntech, B. V., 2020. *Heavy metals*. [online] Available at: <https://www.lenntech.com/processes/heavy/heavy-metals/heavy-metals.htm> [Accessed 12 July 2020].

Lenntech, B. V., 2020. *Nickel – Ni.* [online] Available at: <https://www.lenntech.com/periodic/elements/ni.htm> [Accessed 25 June 2020].

Li, F., Shen, K., Long, X., Wen, J., Xie, X., Zeng, X., Liang, Y., Wei, Y., Lin, Z., Huang, W. and Zhong, R., 2016. Preparation and characterization of biochars from Eichornia crassipes for cadmium removal in aqueous solutions. *PloS one*, 11(2), pp. 1–13.

Liang, J., Liu, M. and Zhang, Y., 2016. Cd(II) removal on surface-modified activated carbon: Equilibrium, kinetics and mechanism. *Water Science and Technology*, 74(8), pp. 1800–1808.

Liu, C., Ngo, H. H. and Guo, W., 2012. Watermelon rind: Agro-waste or superior biosorbent. *Applied Biochemistry and Biotechnology*, 167(6), pp. 1699–1715.

Liu, Y. and Liu, Y.-J., 2008. Biosorption isotherms, kinetics and thermodynamics. *Separation and Purification Technology*, 61(3), pp. 229–242.

Lixandru, M., 2017. *Heavy metals contamination: Causes, symptoms and side effects.* [online] Available at: <https://www.natureword.com/heavy-metals-contamination-causes-symptoms-and-side-effects/> [Accessed 12 July 2020].

Lokhande, R. S., Singare, P. U., Pimple, D. S., 2011. Toxicity study of heavy metals pollutants in waste water effluent samples collected from Taloja Industrial Estate of Mumbai, India. *Resources and Environment*, 1(1), pp. 13–19.

Lokhande, R. S., Singare, P. U. and Pimple, D. S., 2012. Study on physico-chemical parameters of waste water effluents from Taloja Industrial Area of Mumbai, India. *International Journal of Ecosystem*, 1(1), pp. 1–9.

Malaeb, L. and Ayoub, G. M., 2010. Reverse osmosis technology for water treatment: State of the art review. *Desalination*, 267(1), pp. 1–8.

Mallampati, R., Xuanjun, L., Adin, A. and Valiyaveettil, S., 2015. Fruit peels as efficient renewable adsorbents for removal of dissolved heavy metals and dyes from water. *ACS Sustainable Chemistry & Engineering*, 3(6), pp. 1117–1124.

Ministry of Health Malaysia, 2016. *Drinking water quality standards.* [online] Available at: <https://environment.com.my/wp-content/uploads/2016/05/Drinking-Water-MOH.pdf> [Accessed 25 June 2020].

Modak, J. M. and Natarajan, K. A., 1995. Biosorption of metals using nonliving biomass–A review. *Minerals and Metallurgical Processing*, 12, pp. 189–196.

Mohamed, H. S., Soliman, N. K., Abdelrheem, D. A., Ramadan, A. A., Elghandour, A. H. and Ahmed, S. A., 2019. Adsorption of Cd2+ and Cr3+ ions from aqueous solutions by using residue of Padina gymnospora waste as promising low-cost adsorbent. *Heliyon*, 5(3), pp. 1–32.

Mordor Intelligence, 2019. *Avocado market - growth, trends, and forecast (2019 - 2024).* [online] Available at: <https://www.researchandmarkets.com/reports/4773685/avocado-market-growth-trends-and-forecast> [Accessed 10 August 2020].

Munawar, R., Mughal, E. U., Sadiq, A., Mukhtar, H., Zafar, M. N., Mumtaz, M. W., Ahmed, I., Zubair, M., Khan, B. A., Ashraf, J., Yousaf, Z. and Akbar, N., 2018. Biotechnology: A powerful tool for the removal of cadmium from aquatic systems. *Sains Malaysiana*, 47(1), pp. 27–34.

Murithi, G., Onindo, C. O., Wambu, E. W. and Muthakia, G. K., 2014. Removal of cadmium (II) ions from water by adsorption using water hyacinth (Eichhornia crassipes) biomass. *BioResources*, 9(2), pp. 3613–3631.

Nessim, R. B., Bassiouny, A. R., Zaki, H. R., Moawad, M. N. and Kandeel, K. M., 2011. Biosorption of lead and cadmium using marine algae. *Chemistry and Ecology*, 27(6), pp. 579–594.

New Delhi Television Food, 2019. *11 Best avocado recipes | easy avocado recipes.* [online] Available at: <https://food.ndtv.com/lists/10-best-avocado-recipes-745515> [Accessed 6 April 2021].

Othman, N., Mohd-Asharuddin, S. and Azizul-Rahman, M. F. H., 2013. An overview of fruit waste as sustainable adsorbent for heavy metal removal. *Applied Mechanics and Materials*, 389, pp. 29–35.

Papirio, S., Frunzo, L., Mattei, M. R., Ferraro, A., Race, M., D’Acunto, B., Pirozzi, F. and Esposito, G., 2017. Heavy metal removal from wastewaters by biosorption: Mechanisms and modeling. In: E. R. Rene, E. Sahinkaya, A. Lewis, and P. N. L. Lens, eds. 2017. *Sustainable heavy metal remediation.* Cham: Springer International Publishing, pp. 25–63.

Pawar, S., Theodore, T. and Hiremath, P. G., 2019. Syntheis of hydroxyapatite from avocado fruit peel and its application for hexavalent chromium removal from aqeuous solutions – Adsorption isotherms and kinetics study. *Rasayan Journal of Chemistry*, 12(04), pp. 1964–1972.

Podstawczyk, D., Witek-Krowiak, A., Dawiec, A. and Bhatnagar, A., 2015. Biosorption of copper (II) ions by flax meal: Empirical modeling and process optimization by response surface methodology (RSM) and artificial neural network (ANN) simulation. *Ecological Engineering*, 83, pp. 364–379.

Raman, M., 2019. *Ecological nightmare haunts Penang.* [online] Available at: <https://anilnetto.com/environmentclimate-change/penangs-fisheries-and-fisherfolk-in-jeopardy/> [Accessed 5 July 2020].

Rani, M. J., Hemambika, B., Hemapriya, J. and Kannan, R., 2010. Comparative assessment of heavy metal removal by immobilized and dead bacterial cells: A biosorption approach. *African Journal of Environmental Science and Technology*, 4(2), pp. 77–83.

Reich, D., 2016. *What is ion exchange*. [online] Available at: <https://www.fluencecorp.com/what-is-ion-exchange/> [Accessed 20 July 2020].

Rudzinski, W. and Plazinski, W., 2006. Kinetics of solute adsorption at solid/solution interfaces: A theoretical development of the empirical pseudo-first and pseudo-second order kinetic rate equations, based on applying the statistical rate theory of interfacial transport. *The Journal of Physical Chemistry. B*, 110(33), pp. 16514–16525.

Saikaew, W. and Kaewsarn, P., 2009. Cadmium ion removal using biosorbents derived from fruit peel wastes. *Songklanakarin Journal of Science and Technology*, 31(5), pp. 547–554.

Sanusi, K. A., Umar, B. A. and Abdullahi, S., 2015. Biosorption of Cd2+ from aqueous solution using papaya (Carica papaya) seed: Equilibrium and kinetic studies. *Merit Research Journal of Environmental Science and Toxicology,* 3(8), pp. 83–90.

Semerjian, L., 2010. Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated Pinus halepensis sawdust. *Journal of hazardous materials*, 173(1–3), pp. 236–242.

Shazili, N. A. M., Yunus, K., Ahmad, A. S., Abdullah, N. and Rashid, M. K. A., 2006. Heavy metal pollution status in the Malaysian aquatic environment. *Aquatic Ecosystem Health & Management*, 9(2), pp. 137–145.

Shen, L., Liu, Y. and Wang, Z. W., 2009. Biosorption kinetics. In: Y. Liu, and J. L. Wang, eds. 2009. *Fundamentals and applications of biosorption isotherms, kinetics and thermodynamics.* New York, United States: Nova Science Publishers, pp. 119–154.

Shen, L., Wang, Z. W., Fang, S. Q. and Liu, Y., 2009. Biosorption isotherms and thermodynamics. In: Y. Liu, and J. L. Wang, eds. 2009. *Fundamentals and applications of biosorption isotherms, kinetics and thermodynamics.* New York, United States: Nova Science Publishers, pp. 81–118.

Simonin, J.-P., 2016. On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics. *Chemical Engineering Journal*, 300, pp. 254–263.

Smith, B., 2016. Narrative analysis. In: E. Lyons, and A. Coyle, eds. 2016. *Analyzing qualitative data in psychology*. London: Sage, pp. 202–221.

Snyder, H., 2019. Literature review as a research methodology: An overview and guidelines. *Journal of Business Research*, 104, pp. 333–339.

Streefkerk, R., 2018. Primary and secondary sources. *Scribbr*. [online] 20 Jun. Available at: <https://www.scribbr.com/citing-sources/primary-and-secondary-sources/> [Accessed 15 January 2021].

Tan, G., Yuan, H., Liu, Y. and Xiao, D., 2011. Removal of cadmium from aqueous solution using wheat stem, corncob, and rice husk. *Separation Science and Technology*, 46(13), pp. 2049–2055.

Tanasal, A. M., La-Nafie, N. and Taba, P., 2015. Biosorption of Cd(II) ion by dragon fruit peel. *Indonesia Chimica Acta*, 8(1), pp. 18–29.

Tripathi, N., 2017. *The disadvantages of ion exchange.* [online] Available at: <https://sciencing.com/disadvantages-ion-exchange-8092882.html> [Accessed 20 July 2020].

United States Environmental Protection Agency, 2020. *National primary drinking water regulations.* [online] Available at: <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations> [Accessed 25 June 2020].

University of Minnesota Crookston, 2021. *Primary, secondary, and tertiary sources.* [online] Available at: <https://www.crk.umn.edu/library/primary-secondary-and-tertiary-sources> [Accessed 15 January 2021].

Vieira, R. H. S. F. and Volesky, B., 2000. Biosorption: A solution to pollution. *Internatl Microbiol*, 3, pp. 17–24.

Vijayaraghavan, K. and Yun, Y.-S., 2008. Bacterial biosorbents and biosorption. *Biotechnology Advances*, 26(3), pp. 266–291.

VITO, 2020. *Chemical precipitation.* [online] Available at: <https://emis.vito.be/en/bat/tools-overview/sheets/chemical-precipitation> [Accessed 10 July 2020].

Volesky, B. and Holan, Z. R., 1995. Biosorption of heavy metals. *Biotechnol. Prog.*, 11(3), pp. 235–250.

Volesky, B., 1990. *Biosorption of heavy metals.* Florida, United States: CRC Press.

Volesky, B., 2007. Biosorption and me. *Water research*, 41(18), pp. 4017–4029.

Wang, F. Y., Wang, H. and Ma, J. W., 2010. Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent–bamboo charcoal. *Journal of hazardous materials*, 177(1-3), pp. 300–306.

Wang, H., Gao, B., Wang, S., Fang, J., Xue, Y. and Yang, K., 2015. Removal of Pb(II), Cu(II), and Cd(II) from aqueous solutions by biochar derived from KMnO4 treated hickory wood. *Bioresource technology*, 197, pp. 356–362.

Wang, H., Liu, Y., Hu, X., Li, T., Liao, T. and Lu, M., 2014. Removal of cadmium from aqueous solution by immobilized Microcystis aeruginosa: Isotherms, kinetics and thermodynamics. *Journal of Central South University*, 21(7), pp. 2810–2818.

Wang, J. L. and Chen, C., 2009. Biosorbents for heavy metals removal and their future. *Biotechnology Advances*, 27(2), pp. 195–226.

Wang, L. K., Vaccari, D. A., Li, Y., Shammas, N. K., 2005. Chemical precipitation. *Handbook of Environmental Engineering*, 3, pp. 141–197.

Water Quality Association, 2013. *Cadmium.* [online] Available at: <https://www.wqa.org/Portals/0/Technical/Technical%20Fact%20Sheets/2015_Cadmium.pdf> [Accessed 30 June 2020].

World Health Organization, 2011. *Guideline for drinking-water quality*. 4th ed. [pdf] Geneva: World Health Organization. Available at: <http://apps.who.int/iris/bitstream/handle/10665/44584/9789241548151_eng.pdf;jsessionid=E08724B01DEBF746D639045830AB198C?sequence=1> [Accessed 28 June 2020].

Zhang, C., Jiang, Y., Li, Y., Hu, Z., Zhou, L. and Zhou, M., 2013. Three-dimensional electrochemical process for wastewater treatment: A general review. *Chemical Engineering Journal*, 228, pp. 455–467.

Zhang, X., Zhao, X., Wan, C., Chen, B. and Bai, F., 2016. Efficient biosorption of cadmium by the self-flocculating microalga Scenedesmus obliquus AS-6-1. *Algal Research*, 16, pp. 427–433.