



UNIVERSITI TEKNOLOGI MARA

**ADSORPTION CAPACITY OF CADMIUM (Cd) FROM WASTEWATER  
USING CORN COB**

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## ABSTRACT

In the developing world, environmental pollution is becoming a global problem and concern that is caused by the presence of toxic materials such as cadmium. The research aimed was to use low-cost adsorbent such as corn cob wastes in the treatment of industrial wastewater to remove cadmium efficiently. In this research, the parameters of adsorbent dosage, pH of the aqueous solution and different initial metal concentrations were also observed as the factors for the binding of cadmium metal ions at the surface sites of the adsorbent which was the corn cob. To compare the efficiency of the removal using corn cob, it was divided into two samples. One of the samples was treated with 10% hydrochloric acid. The chemical treatment using hydrochloric acid increased the oxygen content of the adsorbent. This treatment encourages cellulose hydrolysis of adsorbent that creates more reactive sites of the adsorbent. Overall, adsorption tests showed that the treated corn with the treatment of the hydrochloric acid resulted in a more efficient process in the removal of cadmium rather than untreated corn cob. The research showed that the removal of cadmium could be achieved at dosage of 3 g/L of treated corn cob (99.43%) and 7 g/L of untreated corn cob (26.47%). For initial metal concentrations, the highest removal efficiency for treated corn cob was at 60 ppm (99.40%) and 20 ppm (50.30%) for untreated corn cob. Besides, treated corn cob was removed at optimum pH 6 at removal efficiency of 76.38% and untreated con cob removed at optimum pH 8 at removal efficiency of 96.58%. The maximum adsorption capacity for cadmium was at 3.31 mg/g. Then, correlation coefficient ( $R^2$ ) of Langmuir was 0.87 and Freundlich was 0.63. Hence, Langmuir isotherm model was better and suited for this research.

## ABSTRAK

Di kebanyakan negara yang membangun pada masa kini, pencemaran alam sekitar telah menjadi satu masalah yang telah membimbangkan seluruh dunia. Hal ini adalah disebabkan oleh pencemaran bahan toksik seperti cadmium. Tujuan penyelidikan ini adalah untuk mengguna pakai sisa buangan dari pertanian seperti sisa tongkol jagung dalam perawatan air sisa industri untuk mengeluarkan cadmium dengan lebih berkesan. Dalam penyelidikan ini, kriteria seperti timbangan berat sisa tongkol jagung, nilai pH air tersebut dan kepekatan awal yang berbeza turut diperhatikan sebagai faktor untuk menyingkirkan kadmium di permukaan penjerap iaitu tongkol jagung. Untuk membandingkan keberkesanan penyingkiran menggunakan sisa tongkol jagung, ia dibahagikan kepada dua sampel. Salah satu sampel telah dirawat dengan 10% asid hidroklorik. Rawatan kimia menggunakan asid hidroklorik ini adalah untuk meningkatkan kandungan oksigen bahan penjerap. Khususnya, rawatan ini menggalakkan hidrolisis selulosa penjerap menjadi lebih reaktif. Secara keseluruhannya, keputusan penyelidikan ini menunjukkan bahawa jagung yang dirawat dengan rawatan asid hidroklorik menghasilkan proses yang lebih baik dalam penyingkiran kadmium daripada air berbanding dengan tongkol jagung yang tidak dirawat. Penyelidikan ini juga telah menunjukkan bahawa penyingkiran kadmium boleh dicapai pada dos 3 g/L untuk tongkol jagung yang telah dirawat (99.43%) dan 7 g/L untuk tongkol jagung yang tidak dirawat (26.47%). Pada kepekatan awal, kecekapan penyingkiran tertinggi untuk jagung yang dirawat adalah pada 60 ppm (99.40%) dan 20 ppm (50.30%) untuk yang tidak dirawat. Selain itu, penyingkiran kadmium telah dicapai pada penyingkiran 76.38% iaitu pada optimum pH 6 untuk jagung yang tidak dirawat, manakala untuk jagung yang telah dirawat, penyingkiran kadmium tertinggi dicapai pada 96.58% pada optima pH 8. Kapasiti penjerapan maksima untuk kadmium adalah pada 3.31 mg/g. Kemudian,  $R^2$  untuk Langmuir model adalah 0.87 manakala untuk Freundlich ialah 0.63. Oleh itu, model isotherm yang lebih sesuai untuk penyelidikan ini adalah Langmuir.

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## TABLE OF CONTENTS

	<b>Page</b>
<b>ABSTRACT</b>	iii
<b>ABSTRAK</b>	iv
<b>ACKNOWLEDGEMENTS</b>	v
<b>TABLE OF CONTENTS</b>	vi
<b>LIST OF TABLES</b>	viii
<b>LIST OF ABBREVIATIONS</b>	x
<b>CHAPTER 1</b>	<b>1</b>
INTRODUCTION	1
1.1 Background	1
1.2 Problem statement	3
1.3 Significance of study	4
1.4 Objectives of study	5
<b>CHAPTER 2</b>	<b>6</b>
LITERATURE REVIEW	6
2.1 Introduction	6
2.2 Pollutant	6
2.2.1 Cadmium	7
2.3 Agricultural wastes	8
2.4 Corn cob	10
2.4.1 Properties of corn cob	11
2.4.2 Modified and treated corn cob	11
2.4.3 Parameters for the adsorption of cadmium	12
<b>CHAPTER 3</b>	<b>15</b>
METHODOLOGY	15
3.1 Preparation of corn cob	15
3.2 Treatment of corn cob	16
3.3 Preparation of chemical	17
3.4 PARAMETERS FOR THE ADSORPTION OF CADMIUM	17
3.4.1 Effect of adsorbent dosage	17
3.4.2 Effect of pH	18
3.4.3 Effect of initial metal concentrations	18
3.4.4 Adsorption isotherm	19
3.5 Adsorption test	21
3.6 Data Analysis	22
<b>CHAPTER 4</b>	<b>23</b>
RESULTS AND DISCUSSION	23

4.1	Effect of modification on the chemical bond of biosorbent	23
4.2	Effect of adsorbent dosage	25
4.3	Effect of pH of the solution	27
4.4	Effect of initial metal concentration	29
4.5	Adsorption capacity	31
4.6	Adsorption isotherm	32
<b>CHAPTER 5</b>		34
<b>CONCLUSION AND RECOMMENDATIONS</b>		34
5.1	Conclusion	34
5.2	Recommendations	35
<b>CITED REFERENCES</b>		36
<b>CURRICULUM VITAE</b>		40

## LIST OF TABLES

<b>Table</b>	<b>Caption</b>	<b>Page</b>
2.3	Methods and efficiency of removal of heavy metals from wastewater	9
4.1	Functional groups that are present in untreated and treated corn cob	23
4.2	Effect of different adsorbent dosage on the removal of cadmium from aqueous solutions	26
4.3	Effect of different initial metal concentration on the removal of cadmium from aqueous solution	25
4.4	Effect of different initial metal concentration on the removal of cadmium from aqueous solution	30
4.5	Comparison of adsorption capacity of different parameters on the removal of cadmium	32



## LIST OF FIGURES

<b>Figure</b>	<b>Caption</b>	<b>Page</b>
3.1	Drying the corn cobs under the sunlight for one hour	15
3.2	Sample dried in the oven after 24 hours	16
3.3	Treatment of sample with 10% HCl	16
3.4	Washing and filtration	17
4.1	FT-IR spectra of untreated corn cob	24
4.2	FT-IR spectra of treated corn cob	24
4.3	Removal efficiency and adsorption capacity of untreated corn cob	26
4.4	Removal efficiency and adsorption capacity of treated corn cob	26
4.5	Removal efficiency and adsorption capacity of untreated corn cob	28
4.6	Removal efficiency and adsorption capacity of treated corn cob	29
4.7	Removal efficiency and adsorption capacity of untreated corn cob	30
4.8	Removal efficiency and adsorption capacity of treated corn cob	31
4.9	Langmuir plot of corn cob adsorbent for Cd	33
4.10	Freundlich plot of corn cob adsorbent for Cd	33

## LIST OF ABBREVIATIONS

- AAS : Atomic Absorption Spectrometry  
FT-IR : Fourier Transform Infrared

# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Heavy metals of Cadmium (Cd), Copper (Cu) and Nickel (Ni) are very known for their dangerous effect and impact on human health and the environment. The main source of these heavy metals is from industry such as mining processes and it leads to heavy contamination as the heavy metals can enter the groundwater such as rivers, sea, lakes, soil, and aquatic system. Some of the heavy metals might be useful for our human body function but our body can only take a small amount of it. The high intake of heavy metals such as drinking contaminated drinking water and foods that have been planted on polluted soil can deteriorate our body system (Ugochukwu *et al.*, 2022). Eventually, when human consumes too much heavy metals, these will lead to cancer disease, chronic effects, or digestive system disease.

The heavy metal that we can take a look at is Cadmium (Cd). Cadmium (Cd) is one of the examples that cause toxicity in our body system and the environment. It is a greater health risk because there is no metabolic degradation of Cd to fewer toxic species and very poor excretion due to a lack of effective chelating agents. The International Agency for Research on cancer has categorised cadmium as a human carcinogen (group I). The

toxicity of Cd can cause oxidative stress, which disrupts the antioxidant system and leads to formation of reactive oxygen species (ROS), affecting the body's immune system (Suhani *et al.*, 2021).

Until today, there are various methods and techniques studied by the researcher and were made to remove heavy metals from wastewater. One of the methods used is an electrochemical treatment such as electrocoagulation and electrodeposition. Another method to remove heavy metals from wastewater using membrane filtration processes. This process involved chemical precipitation and ion exchange. However, all the techniques and methods that have been mentioned above required a high cost and they are not very recommendable as they consume a large and expensive electricity supply. (Azimi *et al.*, 2017).

Considering all the countries in Malaysia are starting to develop and there are more industrial and urban activities that will be done, studies of the potential of agricultural waste to remove heavy metals from wastewater were conducted. Many researchers have done their part in writing a review paper on how to eliminate heavy metals and study the characteristics of the agricultural waste. Agriculture waste is unwanted materials produced by various agricultural operations. The use of this waste is very important because the cost to make the waste as an adsorbent is low (Deepika *et al.*, 2013). These wastes are including peanut husks, coconut shells, vegetables,

corn cob and rice husk. There are many advantages of using agricultural waste such as being environmentally friendly, low cost and enabling the value of the waste on the economy (Lestari *et al.*, 2020). A study found that agricultural waste has chemical bonds that can naturally bind its bond with heavy metals (Abdelfattah *et al.*, 2016a).

In this study, agriculture waste of corn cob will be used as the adsorbent to remove heavy metals from wastewater. Corn cobs are a lignocellulosic compound where it contains 40% cellulose, 36% hemicellulose, and 16% lignin (Lestari *et al.*, 2020). Corn cob also could bind heavy metals at the sites of its surface. Therefore, the objectives of this research are to measure the removal efficiency and adsorption capabilities of corn cob and then to determine the importance of adsorption isotherm and to identify the performance of its model.

## **1.2 Problem statement**

A significant source of environmental pollution is the discharge of contaminated wastewater containing heavy metals from various industries including solid waste disposal, agricultural and industrial activities (Joseph *et al.*, 2019). Due to the characteristics of heavy metals that are non-biodegradable, they can be the source of various diseases for human health such as digestive system diseases (Igwe *et al.*, 2005). Before the industrial wastewater that contain of heavy metals is released into the source of

water (rivers, sea, lake), industries must find a crucial method to remove or decrease the percentage number of toxic metals in the wastewater. Adsorption is an efficient method which has been successfully used in lowering metal concentration (Schneegurt *et al.*, 2001). The development of a low-cost adsorbent is necessary to replace the costly water treatment (Hezam Saeed *et al.*, 2020). Hence in this research, the agricultural waste of corn cob will be treated and modified to increase the efficiency of the adsorbent sites to bind with the heavy metals. By using agricultural waste from corn cob, indirectly it can help to reduce waste and convert waste to more valuable products.

### **1.3 Significance of study**

This research leads to the development of filter material from agricultural waste as a purification product. Material that used as adsorbent from agricultural waste can act as filter material. By making a change to their mechanical properties, we can increase the surface area, surface loading and reactivity of the adsorbent. Besides, the agricultural waste can be easily obtained, abundant and require a very low cost. Since the entire crop's waste is burned to ashes, the production of waste from these crops eventually contributes to global warming (Mohammed *et al.*, 2014). However, we can reuse or recycle the waste from agricultural activities by turning it into an adsorbent in the adsorption process because they can give a high proportion of surface area for the adsorption process to happened. Therefore, the reuse of agricultural waste from agricultural activities

nonetheless can reduce the massive disposal into the environment that will enhance the healthy environment and human health.

#### **1.4 Objectives of study**

The objectives of this study are:

1. To measure the removal efficiency of Cd and adsorption capacities of corn cob.
2. To determine the adsorption isotherm using Langmuir isotherm.
3. To determine the effect of adsorbent dosage, effect of pH and effect of initial metal concentration on untreated and treated corn cob.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Introduction

An increasing number of contaminants, primarily heavy metals and others such as pesticides, pharmaceuticals, petroleum products, and dyes that can dissolve in water are contributing to the issue of global water pollution (Chen *et al.*, 2022). In order to reduce the risk to human health, many researchers have come up with better solutions such as using low-cost adsorbents of agricultural waste to remove the heavy metals from industrial wastewater. In exploring the disadvantages of agricultural waste, there are many potentials for the waste to be reused in many applications that include the removal of heavy metals using these wastes. One of the most important agricultural wastes is corn cob. Around 164 Tg of corn cobs are reportedly produced worldwide each year (Zou *et al.*, 2021). This is because corn is an important food source for many countries as well as a key ingredient in the food industry (Liew *et al.*, 2021).

#### 2.2 Pollutant

A pollutant is a material that is present in concentrations that could be harmful to all the organisms such as humans, plants and animals. Pollutants can come in all shapes and sizes, including nutrients, heavy



metals, dyes, phenols, antibiotics and pesticides. In the last decade, water pollution is becoming a serious threat to most of the growing countries and urban areas and all of these are caused by human activities. (Liu *et al.*, 2022). The treatment of contaminated drinking water becomes ineffective in removing heavy metals due to the pollution from the heavy metals (Joseph *et al.*, 2019). Heavy metals can be defined as any metallic chemical component consisting of relatively high density that is more than 5 g/cm<sup>3</sup> and from the periodic table, they are located in the fourth period (Azimi *et al.*, 2017; Malik *et al.*, 2017). Some toxic heavy metals that are usually found in industrial wastewater are cadmium, copper, lead, cobalt, chromium, arsenic and zinc. All of these metals cannot biodegrade like organic wastes and can accumulate in living tissues where they can lead to serious health problems (Deepika *et al.*, 2013).

### **2.2.1 Cadmium**

Cadmium can be found in a silver-white soft metal and with 90% naturally occurring elements, it is the most abundant metal in the universe (Khan *et al.*, 2022). According to the report, the average natural availability of Cd in the crust of the earth found in that values between 0.1 and 0.5 ppm (Khatun *et al.*, 2022). Due to human activities, there is an increasing number of Cd being produced from industrial activities such as electroplating, alloy, cement and manufacturing batteries. The United Nations Environment Program (UNEP) reported that between 150 and 2600 tonnes of Cd are being discharged into the environment each year

(Khan *et al.*, 2022). When the body of a human had absorbed Cd, it will stay for 20-30 years in the organism's body and can affect the kidneys as well as the liver. After high exposure to Cd, more volume of Cd can be found in the liver, where its half-life is shorter than in the kidney (Souza-Arroyo *et al.*, 2022). Common symptoms that can be studied from the over consumption of Cd are including of abdominal pain, nausea, burning sensation, vomiting, and muscle cramps. Other than that, cadmium poisoning can also result in gastrointestinal tract corrosion, renal damage and coma depending on the route of poisoning (Khatun *et al.*, 2022).

### **2.3 Agricultural wastes**

Agricultural waste can be defined as the trash generated from numerous agricultural activities including waste from farms and poultry houses (Hsu, 2021). Agriculture produced a lot of solid waste and it is the second-largest source of greenhouse gases (GHGs) in the environment. Some examples of agricultural wastes are grape vines, rice husk, sawdust, banana peel, maize cob, peanut husk, coconut shell and vegetables. The need for controlling the wastes from getting out of hand is very important to the global as to prevent the pollution of the environment such as soil and water pollution. Moreover, agricultural wastes can be recycled in many ways to reduce the risk to human health globally in the future. Furthermore, due to their rare chemical composition, sufficient availability, cost-effectiveness and renewability, agricultural wastes can be used as an adsorbent and catalyst for wastewater treatment (Kumar *et al.*, 2023).

Cellulose, hemicellulose and lignin are the three main polymers that can be found in most agricultural wastes. These polymers also consist of other polar organic functional groups such as ether, phenolic, carboxylic, ketones, aldehydes and alcohols that can bind pollutants from wastewater (Kumar *et al.*, 2023). Table 2.3 below shows the method and efficiency of various agricultural wastes that acts as adsorbent to remove heavy metal ions from wastewater.

Table 2.3 Methods and efficiency of removal of heavy metals from wastewater

Method	Efficiency	Advantages	Disadvantages	References
Biomass-based adsorbent	Remove 80% of heavy metals depending on the type of biosorbent used.	Environmental-friendly, low cost and enabling economic value of the biomass waste.	Require a lot of processes to treat biomass adsorbent.	(Lestari <i>et al.</i> , 2020)
Electrocoagulation	The maximum removal of Cr by electrocoagulation was 98.2.	1. A simple and productive technology used to treat water treatment. 2. Environmental-friendly as it uses electrons as clean reagents. 3. There is no need to add chemical additives	Not a reliable method because it has a poor systematic reactor design and problems with electrode reliability.	(Azimi <i>et al.</i> , 2017)
Activated carbon	Able to remove 100% Ni(II) when the adsorbent concentration is 0.25 g and in the pH of 2-5.	A competitive and effective process for the removal of heavy metals in an aqueous solution.	Require a very high cost.	(Orhan and Büyükgüngör, 1993; Azimi <i>et al.</i> , 2017)) (Azimi <i>et al.</i> , 2017)
Rice husk was treated with sulphuric	The maximum removal of chromium was 88%.	Remove ions of chromium ranging from 6-60 mg/L of chromium at pH 5.	A decrease in the adsorption of chromium when the pH of the aqueous	(Deepika <i>et al.</i> , 2013)

acid with CO <sub>2</sub> activation.			solution was above 5.	
Adsorption using palm oil fuel ash	Remove 99% of Cr(IV) ions.	Can effectively remove Cr(IV), Ni(III) and Pb(II) from wastewater.	Not able to remove heavy metals of Zn (II).	(Mohammed <i>et al.</i> , 2014)
Peanut husk	Can remove heavy metal ions completely at the optimum pH which was pH 6. The removal efficiency is 99%, 62%, 30%, 45% and 38% for Pb, Cd, Co, Mn and Ni metal.	An effective bio-sorbent for the removal of Pb <sup>2+</sup> , Cd <sup>2+</sup> , Co <sup>2+</sup> , Mn <sup>2+</sup> , and Ni <sup>2+</sup> .	1. The removal of Mn took the longest time which was 4 hours. 2. When the initial metal ion concentrations increase, the removal of heavy metals are decreasing.	(Abdelfattah <i>et al.</i> , 2016a)

## 2.4 Corn cob

ASEAN countries have been producing the highest percentage of corn for every year and it is increasing year by year. Around 164 Tg of corn cobs are reportedly produced worldwide each year (Zou *et al.*, 2021). In 2014, Indonesia has been confirmed as the country with the most production of corn as corn is an important food supply for the people and a key component of the food industry. Meanwhile, corn can also be utilised to create various industrial products including starch, corn oil and vitamin (Liew *et al.*, 2021). Corn cob is an example of agricultural wastes of corn residue. It can be unique and different from the other residues as corn cob is nutrient-dense and can be very hard to recycle as feed or fertilizer (Choi *et al.*, 2022).

#### **2.4.1 Properties of corn cob**

Corn cob, a naturally occurring biomass resource, has an exceptional mechanical property and a unique layered structure. Through numerical simulation, it was possible to determine the mechanical properties and the impact of characteristics of the corn cob (Zou *et al.*, 2021). A study has been reported that agricultural wastes such as corn cob has natural capabilities of ion-exchange. found that corn cob has an excellent capability to bind those heavy metal ions (Buasri *et al.*, 2012). With a particle size distribution of 0.85-2.00 mm, corn cob has a density of 0.30 g/cm<sup>3</sup>. They contain cellulose, hemicellulose and lignin. The most abundant polymeric material in corn cob is cellulose, which makes up roughly 80% of it (Vaughan *et al.*, 2001).

#### **2.4.2 Modified and treated corn cob**

There are many ways to increase the adsorption capacities of corn cob by modifying and treating the corn cob with some solutions. For example, corn cob that is treated with methanol-FeCl<sub>3</sub> · 7H<sub>2</sub>O contains a hydroxyl bond that could spontaneously bind cations in synthetic waste. The modified corn cob had higher removal percentages of heavy metals from wastewater than the unmodified corn cob (Lestari *et al.*, 2020). In addition, the surface area of the adsorbent is increasing when corn cob is treated with hydrochloric acid. The presence of more oxygenated groups on the

adsorbent surface is due to oxidation and a larger percentage of acidic sites were found on the surface sites. Therefore, the treated corn cob has adsorption capacities higher than untreated corn cob (Deepika *et al.*, 2013).

### **2.4.3 Parameters for the adsorption of cadmium**

#### **2.4.3.1 Effect of pH**

The presence and uptake of heavy metals and their properties are critically influenced by the pH of water or solution (Joseph *et al.*, 2019). This is a very important influencing factor because it is associated with the competition between hydrogen ions and metal ions at the active sites of the adsorbent surface (Ali *et al.*, 2014). Due to competitive adsorption between hydrogen ions and heavy metal cations at low pH, the percentage removal of Cadmium and Nickel increased significantly as the pH value increased (Ibrahim Abdelfattah, 2016b). When the pH increases, the adsorption will also increase because the adsorbent's surface gets more negatively charged and interacts with the positively charged metal ions (Joseph *et al.*, 2019).

#### **2.4.3.2 Effect of initial metal ion concentration**

The quantity of metal ions in an aqueous solution that is available to bind to active surface sites on the adsorbent depends on the initial concentration of the metal ion (Othmani *et al.*, 2022). From the previous study, it shows that when initial metal ion concentration increases, it gives a decrease in the percentage removal of metals (Ibrahim Abdelfattah, 2016b). At the

highest initial metal ion concentration, the number of adsorbate species was more than the number of available adsorbent surface binding sites, hence give a result in a decrease in the removal of metal ions from the aqueous solution (Othmani *et al.*, 2022).

#### **2.4.3.3 Effect of adsorbent dosage**

The rate of cadmium removal is increased when the adsorbent dosage is increased. The removal rate became constant as the dosage is increased because the site of the surface of the adsorbent have been saturated and reduction of available sites in specific area. Further increase in dosage of adsorbent had no effect on the removal of cadmium (Othmani *et al.*, 2022).

#### **2.4.5 Adsorption capacity and isotherm**

Adsorption capacity refers to the maximum amount of adsorbate that can be adsorbed by a given adsorbent. It represents the total quantity of adsorbate molecules that can be accommodated or retained on the surface of the adsorbent under specific conditions, such as concentration. According to Hezam Saeed *et al.* (2020), adsorption isotherms are the relation between the amount of solute being adsorbed and the concentration of the solute in the fluid phase. Adsorption isotherms are crucial to explain the methods of how adsorbates will react with adsorbents. There are two most common isotherm models that are proposed in this research which are by Langmuir and Freundlich.

According to Arul *et al.*, (2023), the Langmuir isotherm model postulates the creation of a single layer of adsorbed solute and is founded on the ideas that metal ions adhere to a set quantity of well-defined sites, with each site able to accommodate one ion. Additionally, the model assumes that all sites possess equal energy levels and that there is no interaction among the adsorbed ions (Arul *et al.*, 2023). Furthermore, the Freundlich isotherm model belongs to a category of models where the substances being absorbed create a single layer on the adsorbent surface. Unlike the Langmuir model, the Freundlich model allows for the possibility of multilayer adsorption (Ehiomogue *et al.*, 2022).



## CHAPTER 3

### METHODOLOGY

#### 3.1 Preparation of corn cob

Corn cob was bought at the area of Matang in Kuching. To remove any other substances and impurities, the corn cobs were washed with distilled water numerous times (Hezam Saeed *et al.*, 2020). The corn cobs were washed three times to remove any substances and impurities. They were cut into small pieces then they were dried under the sunlight for an hour. After that, the small pieces of corn cobs were dried in the oven at 70°C for 24 hours (Kamal *et al.*, 2021). The dried corn cobs were ground using blender and were weighed. Then, the corn cobs were stored in a dry and closed container. A few samples of corn cob were kept without any treatment as the control samples (Fonseca-Correa *et al.*, 2013).



Figure 3.1 Drying the corn cobs under the sunlight for one hour



Figure 3.2 Sample dried in the oven after 24 hours

### 3.2 Treatment of corn cob

A few samples of corn cobs were washed and treated with 10% HCl for 6 hours at 30°C. Then, the treated corn cobs were washed with a last washing which was using distilled water and filtered. Lastly, the treated samples were dried in the oven for 24 hours at 80°C (Ali *et al.*, 2014).



Figure 3.3 Treatment of sample with 10% HCl



Figure 3.4 Washing and filtration

### **3.3 Preparation of chemical**

Preparation of chemical was done by preparing 100 ppm of Cd heavy metal solution from 1000 ppm of stock solution of Cd. The prepared 100 ppm of Cd heavy metal solution was placed in a 100 mL volumetric flask and diluted to mark (Mian, 2022). Both control and treated corn cob samples were used to study the effect of the removal efficiency of heavy metals from the adsorbent.

## **3.4 PARAMETERS FOR THE ADSORPTION OF CADMIUM**

### **3.4.1 Effect of adsorbent dosage**

A constant of 10 ppm of 50 mL of Cd solution were prepared in four different 250 mL conical flasks. The untreated corn cobs were weighed into four different weights which were 1, 3, 5, 7 and 9 g/L and then corn

cob that had been weight was placed into each of the conical flasks (Ibrahim Abdelfattah, 2016b). Then, the mixed solutions of heavy metals and untreated corn cob were stirred in vibrating incubator for one hour (Hashim and Abdullah, 2019). All the above steps were repeated with the sample of treated corn cob. The solutions from mixed solutions of treated and untreated corn cob were kept to test for their absorbance using AAS.

### **3.4.2 Effect of pH**

Firstly, 10 ppm of 20 mL of Cd were prepared in four different 50 mL volumetric flask. The volumetric flask had varying pH of heavy metals which were 4, 6, 8, 10 and 12 by the addition of a few drops of 0.01 molar of sodium hydroxide (NaOH). The solutions then were tested with pH paper indicator. Next, 0.1g of the sample of untreated corn cobs was weighed and had placed them in each of the conical flasks (Hashim and Abdullah, 2019; Igwe *et al.*, 2005). The solutions containing corn cob samples were placed in vibrating incubator for one hour (Hashim and Abdullah, 2019). The mixtures of samples and solutions was kept to test their absorbance using AAS. The above steps were repeated with the sample of treated corn cob.

### **3.4.3 Effect of initial metal concentrations**

From 1000 ppm of Cd solution, 20 ppm to 120 ppm of Cd metal solutions were prepared in 50 mL volumetric flask (Mian, 2022). Next, at optimum

pH 8 of room temperature, 0.1g of treated corn cob was prepared and the samples were mixed with different concentrations of metals at 25 mL of cadmium for one hour of contact time (Hashim and Abdullah, 2019; Ibrahim Abdelfattah, 2016; Lestari *et al.*, 2020). The solutions were kept to test their absorbance using AAS. These procedures were repeated with the samples of untreated corn cob.

#### **3.4.4 Adsorption isotherm**

Adsorption isotherm defined the relationship between the amount of a substance adsorbed onto a solid surface and the concentration or pressure of the substance in the surrounding medium, at a constant temperature. It is a fundamental concept in the adsorption process and plays an important role in understanding the process. This term provides perception into how adsorbate molecules interact with the surface of the adsorbent and how their concentration affects the extent of adsorption (Ibrahim Abdelfattah, 2016b). Isotherm that are used in this study are the Langmuir isotherm and the Freundlich isotherm.

Langmuir isotherm equation:

The Langmuir isotherm assumes a monolayer adsorption on a homogenous surface. Adsorption occurs when surface sites occupied, further adsorption cannot be held. The equation is:

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

In linearized form;

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \left( \frac{1}{C_e} \right) + \frac{1}{q_m}$$

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

Where;

$C_e$  = Equilibrium concentration (mg/L)

$q_e$  = Amount of solid/adsorbate adsorbed per unit weight of adsorbent (mg/g)

$q_m$  and  $K_L$  = Langmuir constants related to adsorption capacity

The value of separation factor can determine the properties of Langmuir constant;

$$R_L = \frac{1}{1 + K_L \times C_0}$$

When the value of  $R_L > 1$ , the characteristics of adsorption process are unfavorable.

When the value of  $R_L = 1$ , it is linear and favorable when the value is  $0 < R_L < 1$  (Abdelfattah, 2016b).

Freundlich isotherm equation:

Freundlich isotherm is an empirical equation that describes heterogeneous adsorption on surfaces with multiple active sites. It presumes that the adsorption capacity of the surface increases with the concentration of the adsorbate. The equation is given as follows:

$$q_e = C_e^{1/n}$$

In linearized form:

$$\ln q_e = \ln KF + \left(\frac{1}{n}\right) \ln C_e$$

Where;

$C_e$  = Equilibrium concentration (mg/L)

$q_e$  = Amount of solid/adsorbate adsorbed per unit weight of adsorbent (mg/g)

$K_F$  = Freundlich constant

$n$  = Characteristic constant for the adsorption under study

### 3.5 Adsorption Test

Adsorption is a process in which a solid is used to remove a dissolved substance from water. It is the attachment of atoms, ions or molecules to the surface of the top layer of material. For the adsorption test, Atomic Absorption Spectrometry (AAS) was used to measure the amounts of heavy metals being adsorbed from the mixture of solutions from Section

3.3. Calibration standards for Cd was obtained before the mixture of solutions were measured.

### 3.6 Data Analysis

The calculation of removal efficiency percentage calculated using the equation given below (Hezam Saeed *et al.*, 2020; Kamal *et al.*, 2021) ;

$$\text{Removal efficiency (\%)} = \frac{C_i - C_e}{C_i} \times 100\%$$

From the equation that were given above;

$C_i$  = Initial concentration (mg/L)

$C_e$  = Final concentration (mg/L)

The difference between the initial concentration of ( $C_i$ ) and the final concentration ( $C_e$ ) was calculated and was used to compute the adsorptive capacity ( $q_e$ ) as the equation given below (Fonseca-Correa *et al.*, 2013) ;

$$q_e = \frac{(C_i - C_e)(V)}{m}$$

$q_e$  = Adsorption capacity (mg/g)

$m$  = Mass of the adsorbent (g)

$V$  = Volume of the solution (L)



## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Effect of modification on the chemical bond of biosorbent

The chemical bonds for both untreated and treated corn cobs were characterized using FT-IR. Figure 4.1 and Figure 4.2 show the FT-IR spectra of the corn cobs before and after the treatment using hydrochloric acid. Table 4.1 shows the functional groups that are present in untreated and treated corn cob based on the FT-IR spectra that are obtained in Figure 4.1 and Figure 4.2. Figure 4.1 shows that the functional group of O-H has medium intensities, meanwhile after the treatment, intensities of O-H group increased. Liu *et al.*, (2022) stated that this is because of the glycosidic bonds of hemicellulose and cellulose broken down to carboxylic groups. With the treatment of acidification, biosorption of metal ions can be increased in the presence of carboxylic acid (Syeda *et al.*, 2022).

Table 4.1 Functional groups that are present in untreated and treated corn cob

Functional group	FT-IR spectra for untreated corn cob (cm <sup>-1</sup> )	FT-IR spectra for treated corn cob (cm <sup>-1</sup> )	References
O-H stretching	3288 (medium, broad)	3357 (strong, broad)	Deepika <i>et al.</i> , 2013
C=O stretching	1738	-	Ibrahim Abdelfattah <i>et al.</i> , 2016a
C=C stretching	1638	1629	Ibrahim Abdelfattah <i>et al.</i> , 2016a

C-O stretching	1234	1247	
O-H bending	1375	-	
S=O stretching	1033	-	Fonseca-Correa <i>et al.</i> , 2013
C-H stretching	2924	-	
C-N stretching	-	1044	Syeda <i>et al.</i> , 2022

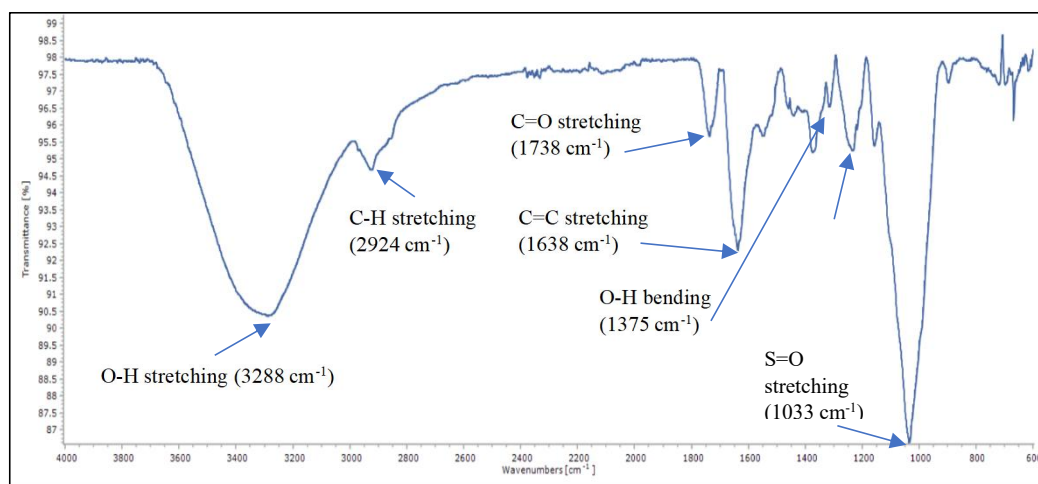


Figure 4.1 FT-IR spectra of untreated corn cob

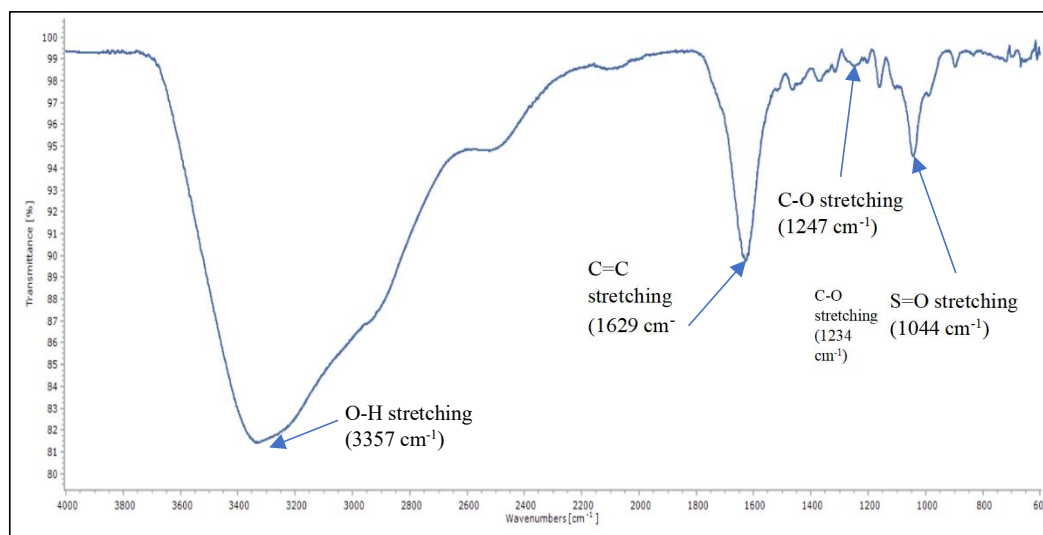


Figure 4.2 FT-IR spectra of treated corn cob with hydrochloric acid (10% HCl)

## 4.2 Effect of adsorbent dosage

The effect of adsorbent doses on the adsorption capacity of cadmium from solution is shown in Table 4.2, Figure 4.3 and Figure 4.4. Adsorbent dosage is one of the factors that can affect the removal process of cadmium from solution. As we can see from Table 4.2, removal rate of cadmium is increased when the dosage of the adsorbent is raised from 1 g/L to 3 g/L and slightly increased for 5 g/L and 7 g/L for untreated corn cob. Abdelfattah (2016b) said that the increase of adsorbent dosage resulting in the decreased of metal ions adsorption capacity (Figure 4.3). The adsorption site was believed to remain unsaturated during the adsorption reaction due to the non-saturation of the adsorption active sites.

Removal rate of cadmium for treated corn cob is also increasing with the adsorbent dosage from 1 g/L to 3 g/L and then the removal efficiency is dropped at dosage of 5, 7 and 9 g/L. These can show that treated corn cob has more optimum performance in removing cadmium from solution with the dosage of 3 g/L as the removal efficiency is 99.43%. However, the removal efficiency became constant for the dosage 5 g/L and above as the adsorbent surface became more saturated with cadmium ion that they were not able to adsorb or bind more heavy metal ions. Any further addition in the dosage of the adsorbent will not cause any changes in the removal process (Hezam Saeed *et al.*, 2020). According to Abdelfattah (2016b), metal ions of cadmium need to be in contact with the biosorbent for longer shaking duration to achieve better and complete removal efficiency.

Table 4.2 Effect of different adsorbent dosage on the removal of cadmium from aqueous solutions

Dosage (g/L)	Removal efficiency on untreated corn cob (%)	Removal efficiency on treated corn cob (%)
1	23.22	26.37
3	25.93	99.43
5	26.43	36.08
7	26.47	25.89
9	26.30	25.80

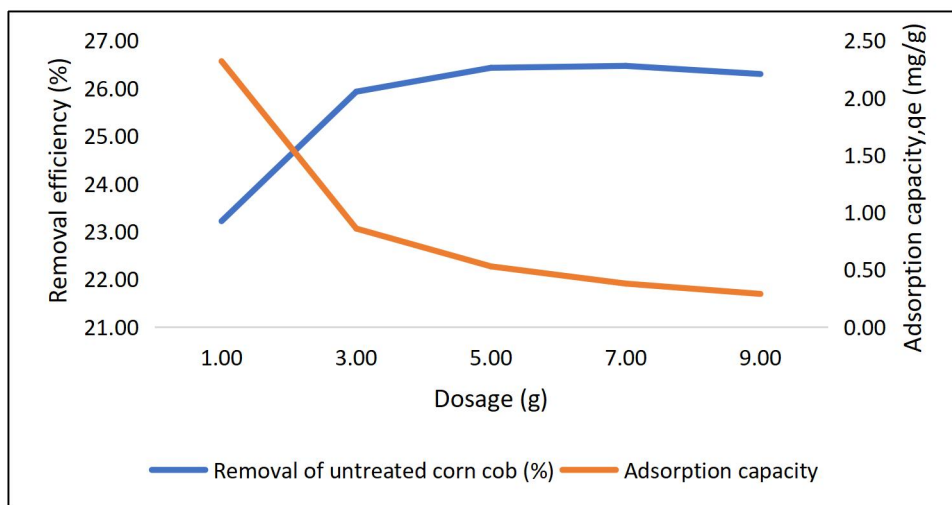


Figure 4.3 Adsorption capacity of untreated corn cob

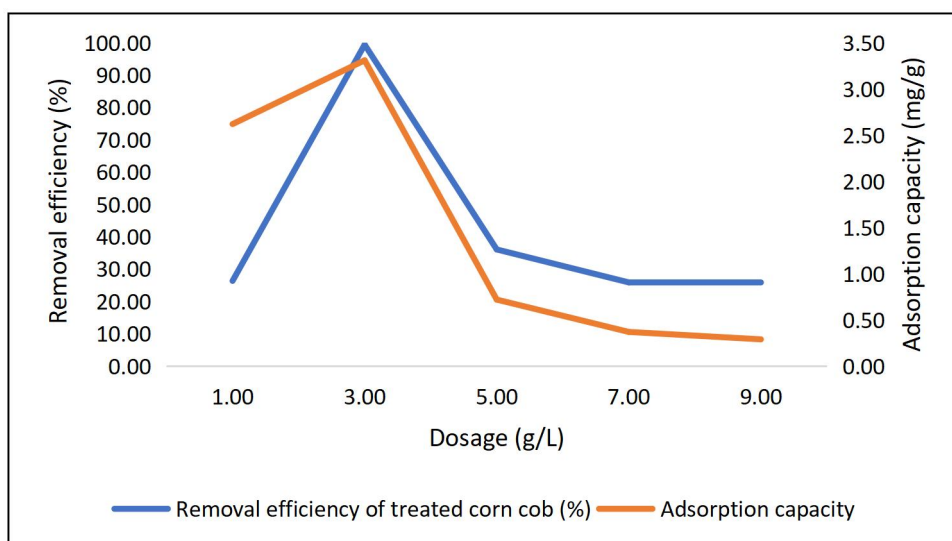


Figure 4.4 Adsorption capacity of treated corn cob

### 4.3 Effect of pH of the solution

Figure 4.5 and Figure 4.6 illustrates how the pH of the solution significantly affects the uptake of heavy metals because it affects the adsorbent's surface charge, degree of ionisation, and speciation of the adsorbate (Arul *et al.*, 2023). For untreated corn cob, the metal uptake increases with increasing pH from pH 4 until it reaches the maximum uptake which is on the pH 6 which is the optimum pH. Cadmium was barely absorbed at pH levels below 6, most likely because of the high number of hydrogen ions competing for the few available adsorption sites on the adsorbent surface. Furthermore, Hezam Saeed *et al.* (2020) stated that cadmium ions are easily absorbed onto the biosorbent surface because the electronegative metal ions have a larger charge density. However, the high concentration of OH ions decreased the removal efficiency of metal ions at higher pH which is more than pH 6 (Hezam Saeed *et al.*, 2020).

Meanwhile, for treated corn cob, the removal efficiency is 96.58% at pH 8 which is its optimum pH. Both untreated and treated corn cob declines after reaching their maximum adsorption of heavy metals on their optimum pH. Heavy metal removals levels normally decline in lower acidic solution and higher basic solution. This is because of the competition between metal ions at adsorption sites, whereas adsorbent-metal ions attraction also declines due to the more positively charged adsorbent surface at higher H<sup>+</sup> concentrations. Moreover, the surface area

became more negatively charged when pH increases that can increase the availability of metal uptake. However, upon increasing the pH further which is more than pH 8, there appears to be a decrease in absorption, which could be due to the presence of OH ions, that create a hindrance effect on the absorption of metal ions to adsorbent (Ibrahim Abdelfattah, 2016b). Therefore, Arul *et al.* (2023) said that at a lower pH which is below than 6, the absorption of cadmium ions are insignificant due to the presence of a substantial number of hydrogen ions, which competed with the metal ions for the available adsorption sites. At higher pH values, it is impossible to carry out adsorption process as the presence of metal forms in a solution can become a significant factor. The increase in the removal of cadmium related to the reduction in solubility and the formation of solid metal hydroxide precipitates (Arul *et al.*, 2023). Ibrahim Abdelfattah *et al.* (2016b) stated that the adsorption capacity of corn cob was based on the pH value of solution.

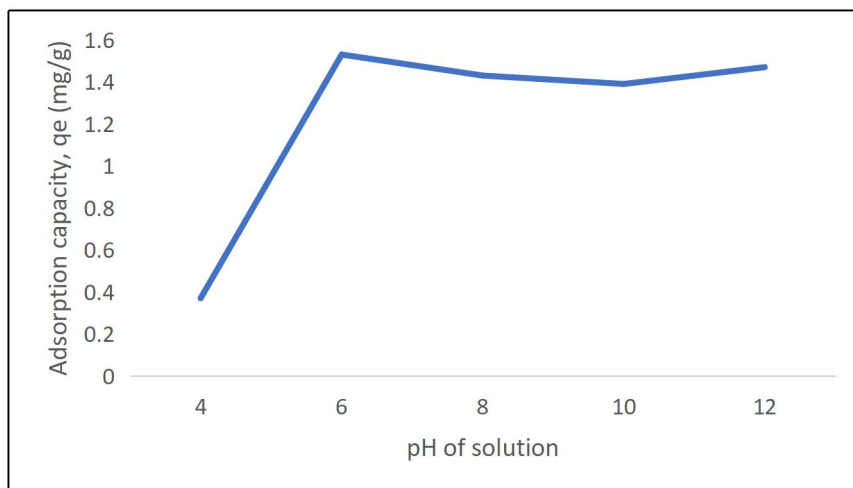


Figure 4.5 Adsorption capacity of untreated corn cob

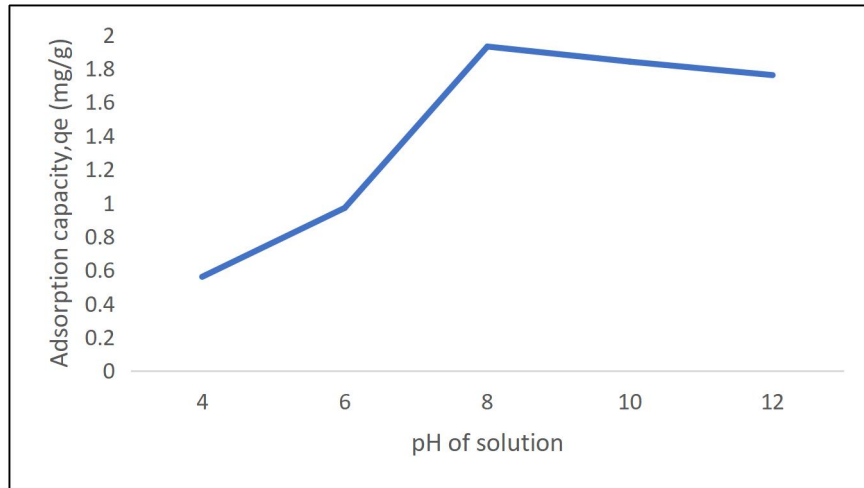


Figure 4.6 Adsorption capacity of treated corn cob

#### 4.4 Effect of initial metal concentration

The behaviour of metal ion to bind at the surface of the adsorbent was investigated with different initial metal concentrations which are 20, 40, 60, 80, 100 and 120 ppm at optimum pH 8. Based on the parameters on the effect of pH, pH 8 has the best removal efficiency on the removal of heavy metals from solution. The result that are shown in Figure 4.7 shows that the increase in metal concentrations will also increase in the adsorption capacity of cadmium from solution. The maximum removal of cadmium for untreated corn cob is only 50.30% and the maximum removal of treated corn cob is 99.4%. From the result shown above, treated corn cob is more effective in removing cadmium ion from the solution with different initial metal concentration. Since the research was using optimum pH 8 on this parameter, this might be the factor of the result that untreated corn cob has lower efficiency removal of heavy metals as its optimum

removal is at pH 6. Therefore, the removal efficiency decreases with the increase in initial metal concentrations.

Table 4.4 Effect of different initial metal concentration on the removal of cadmium from aqueous solution

Initial metal concentration (mg/L)	Removal efficiency of untreated corn cob (%)	Removal efficiency of treated corn cob (%)
20	50.30	98.30
40	44.64	98.90
60	36.33	99.40
80	31.25	98.16
100	30.10	97.77
120	26.43	96.71

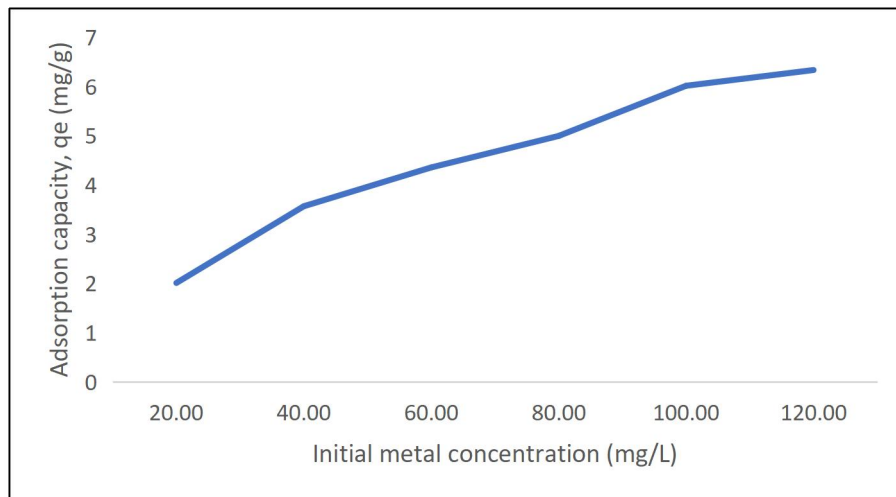


Figure 4.7 Adsorption capacity of untreated corn cob



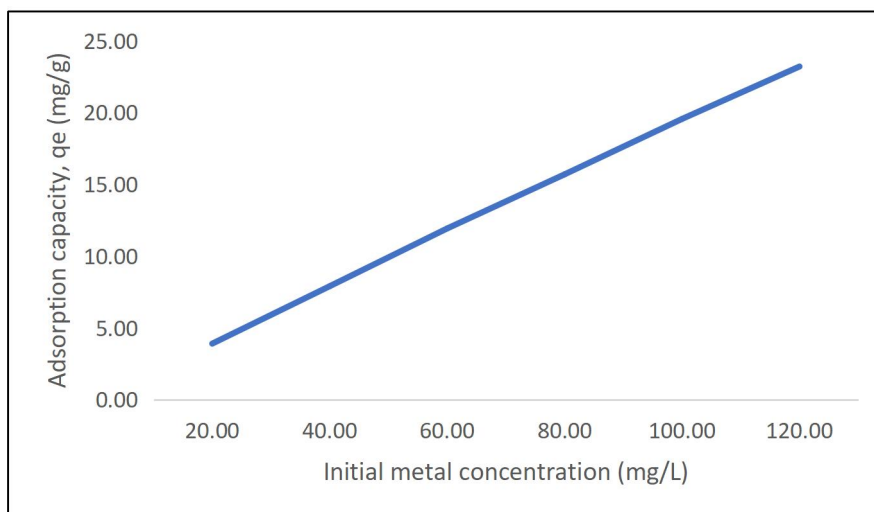


Figure 4.8 Adsorption capacity of treated corn cob

#### 4.5 Adsorption capacity

The relationship between removal efficiency and adsorption capacity of heavy metal removal depends on various factors as shown in the Table 4.5. For adsorbent dosage, the increase in the dosage decrease in removal efficiency as well as the adsorption capacity. Abdelfattah (2016b) said that the increase of adsorbent dosage resulting in the decreased of metal ions adsorption capacity. Next, at optimum pH, it has the highest removal efficiency which also influences the adsorption capacity to increase. Meanwhile, for initial metal concentrations, when the initial metal concentration increases, the adsorption capacity also increases. In general, a higher adsorption capacity leads to a higher potential for removal efficiency. However, other factors also can influence the relationship between adsorption capacity and removal efficiency such as the contact time between adsorbent and the solution and temperature (Ibrahim Abdelfattah, 2016b).

Table 4.5 Comparison of adsorption capacity of different parameters on the removal of cadmium

Parameters	Sample	Removal efficiency (%)	Adsorption capacity (mg/g)
<b>Effect of adsorbent dosage</b>	Treated 1 g/L	26.37	2.62
	Treated 3 g/L	99.43	3.31
	Treated 5 g/L	36.08	0.72
	Treated 7 g/L	25.89	0.37
	Treated 9 g/L	25.80	0.29
<b>Effect of pH</b>	Treated pH 4	28.07	0.56
	Treated pH 6	48.64	0.97
	Treated pH 8	96.58	1.93
	Treated pH 10	91.80	1.84
	Treated pH 12	87.83	1.76
<b>Effect of initial metal concentration</b>	Treated 20 mg/L	97.77	3.91
	Treated 40 mg/L	98.88	7.91
	Treated 60 mg/L	99.42	11.93
	Treated 80 mg/L	98.13	15.7
	Treated 100 mg/L	97.80	19.56
	Treated 120 mg/L	96.73	23.21

#### 4.6 Adsorption isotherm

Langmuir isotherm model postulates the creation of a single layer of adsorbed solute and is founded on the ideas that metal ions adhere to a set quantity of well-defined sites, with each site able to accommodate one ion (Arul *et al.*, 2023). Additionally, the model assumes that all sites possess equal energy levels and that there is no interaction among the adsorbed ions (Arul *et al.*, 2023). To compare between the Langmuir isotherm model and Freundlich isotherm model, it showed that the data is more suitable with the Langmuir isotherm model as the regression coefficients ( $R^2$ ) is 0.8368. The value of  $R^2$  of Freundlich is smaller than  $R^2$  of Langmuir, hence, Freundlich did not suited the best for these experimental results.

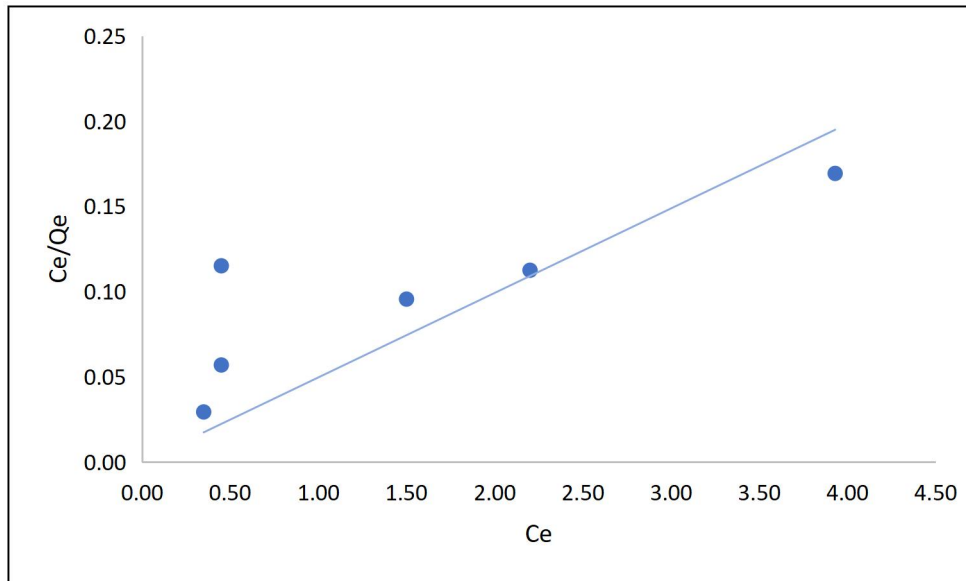


Figure 4.9 Langmuir plot of corn cob adsorbent for Cd

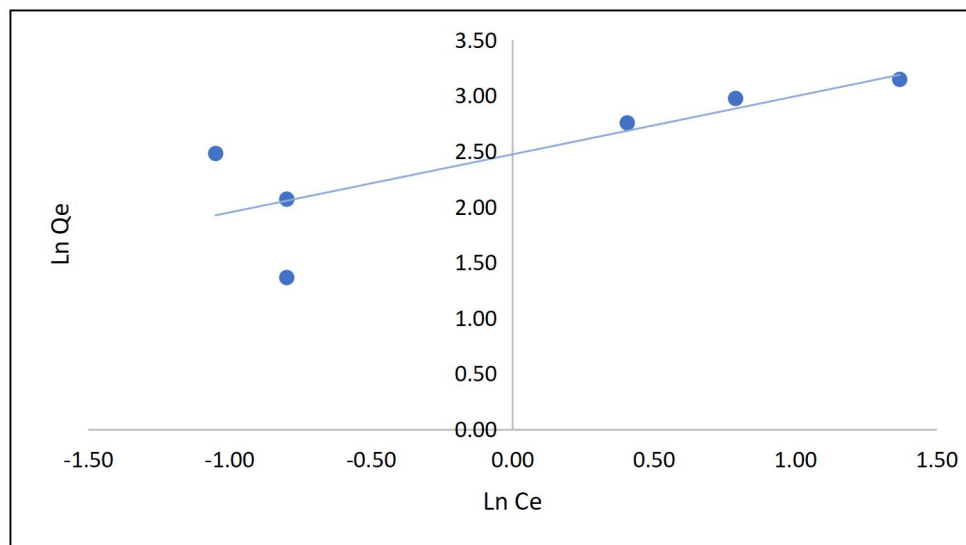


Figure 4.10 Freundlich plot of corn cob adsorbent for Cd

## CHAPTER 5

### CONCLUSION AND RECOMMENDATIONS

#### 5.1 Conclusion

In this research, corn cob biomass was applied as an adsorbent for the removal of heavy metal of cadmium ions from aqueous solution. The experimental results support the performance of treated corn cob biomass as an adsorbent in removing toxic Cd ions. The treatment and modifications of chemical bond in corn cob by using hydrochloric acid attribute to enhance the stability of and durability of the adsorbent. It is also can enhance the adsorbent's affinity and capacity to adsorb target toxic heavy metals or pollutants that are presence in aqueous solution. In addition, this can increase the binding of metal ions at the active sites of the adsorbent surface area. This research also reveals that the dependency of the factor pH of aqueous solution gave a good removal efficiency on the optimum pH 8 for treated corn cob which it removed 96% of the heavy metal cadmium from the solution. The removal efficiency decreases as the adsorbent dose increases, while the removal of cadmium increases as the initial metal concentration increases. Besides, the study of the adsorption isotherm discovered that the experimental data aligned better with Langmuir isotherm model.

## **5.2 Recommendations**

This research has explored various effects that can contribute to eliminate heavy metal from aqueous solution by using the waste of corn cob. Based on the experimental results, the highest removal efficiency is 99.4% at the initial concentration of 60 ppm. It can be concluded that corn cob is an efficient and cost-effective adsorbent for wastewater treatment. Given the sustainable and environmentally friendly biosorbent, it provides potential and interesting qualities for pollution removal. Furthermore, after modifications of biosorbent, it exhibits exceptional adsorption capabilities and performances. For upcoming research and studies, mixed pollutants can be used to gain a better knowledge of the performance of corn cob in real industrial wastewater. In addition, study on the making of corn cob as one of the biosorbent on the filter of water purification can be done. This can be one of the efficient methods to provide safe drinking water as it also can remove toxic heavy metal that might have been present in the drinking water as well as remove contaminants and bacteria. Hence, it is an effective-cost preparation as corn cob is one of the low-cost adsorbents and easy to obtain and prepare.

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# ***CURRICULUM VITAE***

## **A. Personal profile**

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## **A. Hobbies and interests**

I enjoy travelling to other places and love to learn new things at new cities. During my free time, I like to watch movies and dramas that have genre of romantic comedy and horror. I also enjoy listening to some music while doing my work.

## **B. Academic qualifications**

	Area	Institution	Year awarded
Degree B. Sc. (Hons.)	Chemistry and Management	Universiti Teknologi MARA, Malaysia	2023
Diploma	Science (Physics)	Universiti Teknologi MARA, Malaysia	2020
S.P.M	Science	SMK Oya, Dalat	2016

### C. Work experiences

Post	Place	Year
Skim Khidmat Pelajar (SKP)	Unit Pengurusan Kolej Kediaman Seri Pinang, UiTM Kampus Samarahan 2, Sarawak	2020
Sales Assistant	Goglobal Gadget, Gala City, Jalan Tun Jugah, Kuching, Sarawak	2022
Skim Khidmat Pelajar	Unit Pengurusan Kolej Kediaman Seri Pinang, UiTM Kampus Samarahan 2, Sarawak	2023

### D. Related experiences

Post	Place	Year
Setiausaha Agung for Jawatankuasa Perwakilan Kolej (JPK)	Kolej Kediaman Seri Pinang, UiTM Kampus Samarahan 2	2021-2023
Exco Keusahawanan (JPK)	Kolej Kediaman Seri Pinang, UiTM Kampus Samarahan 2	2019 - 2021
Pengawas Bendahari Kelab Bola Jaring	SMK Oya, Mukah	2016
Ketua AJK Kadet Remaja Sekolah	SMK Oya, Mukah	2015
	SMK Oya, Mukah	2014

### E. Awards

Type	Name of award	Year
Certificate	Dean's List Award (2018), Universiti Teknologi MARA, Malaysia	15 <sup>th</sup> December 2018
Certificate	Dean's List Award (2019), Universiti Teknologi MARA, Malaysia	21 <sup>st</sup> May 2019
Certificate	Dean's List Award (2020), Universiti Teknologi MARA, Malaysia	6 <sup>th</sup> February 2020

Certificate

Dean's List Award (2021),  
Universiti Teknologi MARA,  
Malaysia

12<sup>nd</sup> March 2021