UTILIZATION OF CORN COB AS A LOW COST BIOSORBENT FOR THE REMEDIATION OF CARBOFURAN

by

EZRA ATHIRA BINTI YAHYA

A dissertation submitted in partial fullfilment of
the requirements for the
Degree of Bachelor Health Sciences (Hons) (Environmental and Occupational Health)

JUNE 2014

CERTIFICATE

This is to certify that the dissertation entitled 'Utilization of Corn Cob as a Low Cost Biosorbent for the Remediation of Carbofuran' is the bonafide record of research work done by Ezra Athira binti Yahya, Matric Number 109506 during the period of July 2013 to June 2014 under my supervision. I have read this dissertation and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation to be submitted in partial fulfilment for the degree of Bachelor of Health Science (Hons) (Environmental and Occupational Health). Research work and collection of data belong to the Universiti Sains Malaysia.

APPROVAL PAGE

This is to certify that I have read this dissertation and that in my opinion it conforms to acceptable standards of scholarly presentation and of fully adequate, in scope and quality, as a dissertation submitted in partial fulfilment for the degree of Bachelor of Health Sciences (Hons) (Environmental and Occupational Health).

DECLARATION

I hereby declare that this dissertation is the result of my own investigations, except where otherwise stated and duly acknowledged. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at Universiti Sains Malaysia or other institutions.

ACKNOWLEDGEMENT

First of all, I am thankful to Almighty Allah, most Gracious, who in His infinite mercy has guided me to complete this study.

Special thanks to School of Health Sciences and School of Engineering Campus, Universiti Sains Malaysia (USM) for the support and trust given to me in preparing the 'Utilization of Corn Cob as a Low Cost Biosorbent for the Remediation of Carbofuran' for the undergraduates in the programme of Environmental and Occupational Health, School of Health Sciences, USM. I am deeply thanked to Dr Foo Keng Yuen for the truly insightful comments and suggestions to help the progression and smoothness of this final year project.

A great appreciation also goes to the my fellow friends, Ain Nabila Noridan, Alia Amira Yusof, Ho Xiaojun, Mohamad Radhi Amonodin, Nur Syuhada Sabaruddin, Nurhaniza Harun, Nazhatul Ezzaty Ali, Nur Fatihah Ali, Siti Rohana Johari and Wan Hazwani Wan Mohammad Roslan, and special thanks to my beloved parents which Mr Yahya Musliman and Mrs Rosiah Kanang who always understand and support me in any unconditional situation. Finally I apologize to all other who helped me in various ways directly or indirectly during the completion of my final year project.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AC	Activated Carbon
ASAP	Accelerate Surface Area and Porosimetry System
BET	Brunauer-Emmett-Teller
EA	Elemental Analysis
EPA	Environmental Protection Agency
et al.,	*et alia (and others)*
etc.	et cetera (and the rest)
EU	European Union
FAO	Food and Agriculture Organization
FAOSTAT	The Statistic Division of the FAO
FT-IR	Fourier Transform Infrared Spectroscopy
GHG	Greenhouse Gas
MR	Modification Ratio
OECD	Organization for Economic Co-operation and Development
RMSD	Root Mean Square Deviation
SBET	Specific surface area Brunauer-Emmett-Teller
SEM	Scanning Electron Microscope
UNEP	United Nations Environment Programme
UNIDO	United Nations Industrial Development Organizations
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
VS	Volatile Solid
WHO	World Health Organization

LIST OF SYMBOLS

a_t	equilibrium binding constant
b_t	heat of adsorption
bu/acre	bushels per acre
C_o	initial concentration
C_e	concentration at equilibrium
g/cm^3	gram per cubic centimetre
J/mol	Joules per mole
J/molK	Joules per mole Kelvin
K	Kelvin
K_D	distribution coefficient
K_f	Freundlich constant
K_L	Langmuir constant
km^2	kilometre
kPa	kilopascals
lbs/acre	pounds per acre
LD_{50}~	Lethal Dose, 50%
L/mg	Litre per milligram
M	Molecular weight
M_c	Moisture content
mg/mol	milligram per mole
mg/L	milligram per litre
mm	millimetre
nm	nanometre

q_e	amount at equilibrium
Q_m	maximum adsorption capacity
R	universal gas constant
R^2	determination of coefficient
R_L	separation factor
rpm	revolutions per minute
sq.km	square kilometre
T (°C)	Temperature (Celcius)
V	Volume
W (g)	Weight (gram)
wt (%)	weight percentage
$\mu g/dm^3$	microgram per cubic decimetre
µg//L	microgram per litre
µm	micrometre
ΔH^o	enthalphy
ΔG^o	free Gibbs energy
ΔS^o	entrophy
1/n	adsorption intensity
%	percentage
>	greater than
<	less than
=	equal

PENGGUNAAN TONGKOL JAGUNG SEBAGAI PENJERAP BIOLOGI KOS RENDAH UNTUK PENYINGKIRAN RACUN PEROSAK CARBOFURAN

ABSTRAK

Kajian larutan akues ke atas tongkol jagung sebagai bahan semula jadi kos rendah sebagai penjerap biologi untuk penyingkiran carbofuran telah dijalankan. Kaedah yang dijalankan untuk mengenalpasti agen modifikasi, kadar nisbah modifikasi, dos penjerapan, masa interaksi dan kepekatan awal, pH dan suhu penjerapan. Hasil kajian menunjukkan sodium karbonat agen modifikasi terbaik, dengan penjerapan pengambilan carbofuran sebanyak 142.0 mg/g. Kadar nisbah modifikasi, 1.5 dikenal pasti sebagai nisbah yang terbaik. Pada dos 0.3 g, pengambilan jerapan adalah optimum dengan penyingkiran jerapan sebanyak 148.82 mg/g dan 74.77%, apabila masa interaksi meningkat, kepekatan awal menunjukkan peningkatan kepada pengambilan penjerapan dan kecekapan penyingkiran. Pada pH 2.0, penyingkiran carbofuran adalah maksimum. Spektra FTIR menunjukkan kehadiran kumpulan fungsi terikat seperti OH-, $-CH_2$ dan $-CH_3$, C = O, C = C, NH, simetri dan ansimetri COH, COC dan glykosidik C1- H dengan getaran bentuk cincin terhadap penjerap ke atas agen modifikasi Na_2CO_3. Analisis elemen C, O, H, N dan S menunjukkan keputusan 48.77%, 42.89%, 7.32%, 1.99%, dan 0.03%, manakala analisis anggaran bagi kandungan abu, resapan pepejal dan kandungan kelembapan adalah 7.56%, 86.53% dan 5.91%. Antara model isoterma yang diuji ialah model Langmuir di mana menunjukkan keputusan korelasi, R^2 yang lebih baik dan RMSD masing-masing ialah, 0.998 dan 0.639, dengan kapasiti lapisan mono penjerapan maksimum 149.15 mg/g pada suhu operasi 30°C. $\Delta G°$ adalah -2.322 J/mol, -0.893 J/mol, dan 0.377 J/mol; $\Delta H°$ dan $\Delta S°$ adalah masing-masing -42.23 J/mol dan -135.10 J/mol. Nilai negatif $\Delta H°$ menunjukkan sifat eksotermik dalam interaksi penjerapan. Keputusan ini boleh membantu dalam membentuk sistem mod kelompok untuk penyingkiran carbofuran dengan menggunakan cairan sisa air. Hasil kajian menunjukkan tongkol jagung sebagai penjerap biologi kos rendah dan mesra alam berbanding dengan adsorben komersial lain.

UTILIZATION OF CORN COB AS A LOW COST BIOSORBENT FOR THE REMEDIATION OF CARBOFURAN

ABSTRACT

The potential of corn cob as a natural low-cost biosorbent for the removal of carbofuran from the aqueous solution has been investigated. The effects of modification agents, modification ratio, adsorbent dosage, initial concentration and contact time, pH and temperature on the adsorption process were carried out. Sodium carbonate was identified as the best modification agent, with the adsorption uptake for carbofuran of 142.0 mg/g respectively. Modification ratio (MR) of 1.5 was identified as the best MR. The optimum adsorptive uptake and adsorptive removal of carbofuran are denoted at 148.82 mg/g and 74.77%, respectively at the adsorbent dosage of 0.3 g increasing the initial concentration of showed an increase of adsorption uptake and removal efficiency with prolonging the contact time. Maximum carbofuran removal was observed at pH 2.0. The physical and chemical characterization was carried out, FTIR spectra indicated the presence of bonded OH-, $-CH_2$ and $-CH_3$, C=O, C=C, NH, asymmetric and symmetric C-O-H, C-O-C and glycosidic C1-H deforming with ring vibration on the Na_2CO_3 modified adsorbent. The elemental analysis illustrated that the content of C, O, H, N and S was 48.77%, 42.89%, 7.32%, 1.99%, and 0.03% respectively, while proximate analysis revealed that the ash, volatile and moisture content was 7.56%, 86.53% and 5.91%. Among the tested isotherm model, Langmuir model provided the better correlation, R^2 and RMSD of 0.998 and 0.639, respectively, with a maximum monolayer adsorption capacity of 149.15 mg/g at the operating temperature of 30°C. The calculated $\Delta G°$ was -2.322 J/mol, -0.893 J/mol, and 0.377 J/mol; $\Delta H°$ and $\Delta S°$ were -42.23 J/mol and -135.10 J/mol, respectively. The negative value of $\Delta H°$ indicated the exothermic nature of the adsorption interaction. These results can be helpful in designing a batch mode system for the removal of carbofuran from dilute wastewater. The findings revealed the potential of modified corn cob as a low economical and eco-friendly biosorbent as compared to the commercial adsorbents.

CHAPTER ONE

INTRODUCTION

1.1 The global generation and waste management problem of agricultural residue.

At the beginning of the 21st century, there were about 129.7 million hectares (sq. km) of land area was used for agricultural application and now it has reduced to 49.1 million hectares (sq. km), accounts for which 37.6% of land area in year 2011 (FAO, 2013; The World Bank Group, 2013). The loss of agricultural land area has been concentrated in developing countries, driven by the growing demand for timber and agricultural land and exacerbated by the weak monitoring institutions. Data presented here highlights the indicators on agricultural input, output, and productivity; rural population, and land use. But depletion and degradation of land and water pose serious challenges to produce enough food and other agricultural products to sustain livelihood here and meet the needs of urban populations.

The global agricultural production is expected to grow 1.5% a year on average over the coming decade, compared with annual growth of 2.1% between year 2003 and 2012 (FAO, 2011; OECD, 2011). Agricultural is the main source of income and employment for the 70% of the world's poor that lived in rural areas (The World Bank Group, 2014). Figure 1.1 represents the world production in million tonnes of major agricultural crops (FAOSTAT, 2013) which is dominant by sugarcane, corn, rice paddy and wheat. The analysis of data in Figure 1.1 provides an outlook estimate of the annual biomass production yield from ten major agricultural crops and is presented. According to UNEP's findings, 5 billion metric tons of biomass is generated every year from agriculture. If properly managed, this agricultural biomass could be converted into a high valuable commodity.

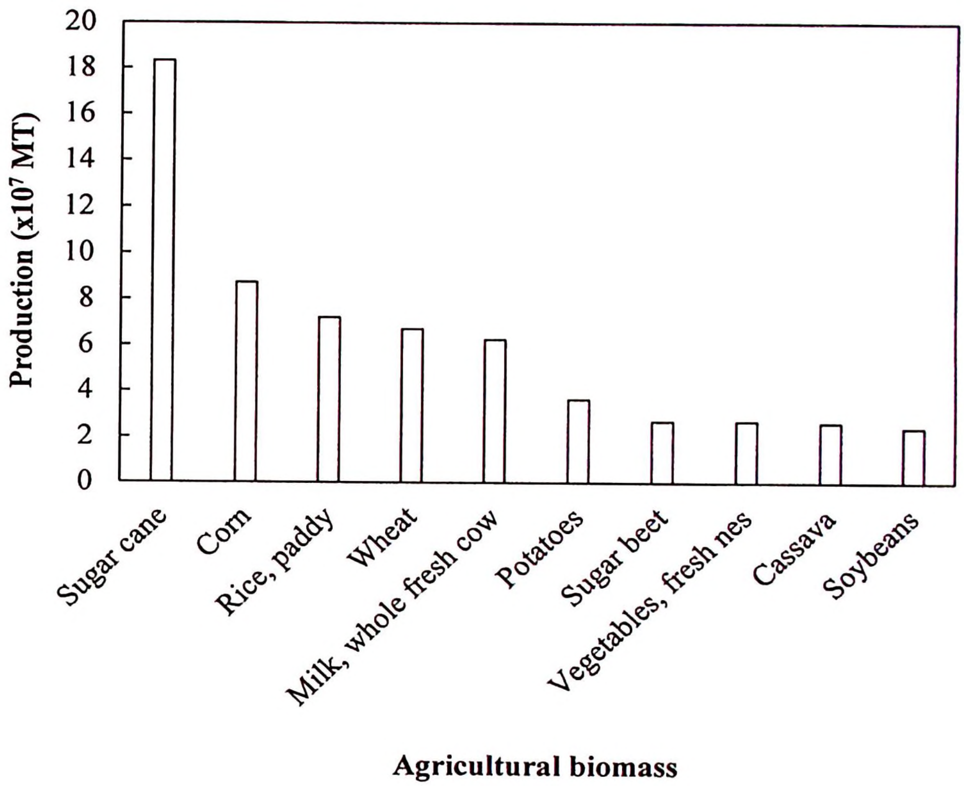


Figure 1.1: The world productions of major agricultural crops 2012 (FAO, 2013).

Over the years, several technologies have been developed to recycle this biomass and competition for these resources is increasing with the growth of population, cities, and demand for food. As a result, the rapid increase of volume and types of waste agricultural production in the wake of population growth and improved living standards, from population and economic growth has created the waste generation management problem globally (UNEP, 2011). The waste generation management becoming a serious problem, when GHG emission is accompanied with methane, leachate, and open burning generating CO_2 and transport with other pollutants. Hence, improper management of waste agricultural biomass is contributing to the local air pollution, water and soil contamination, and climate change (UNEP, 2013).

Climate change is altering the patterns of rainfall and temperature that agriculture could depend on. Global environmental changes have contributed to the effects on agricultural productivity, such as water availability and the length of the growing season. While changes in temperature and precipitation patterns may benefit agriculture in some areas, they may restrict it in others, and enhance the risk of hunger and famine, particularly in poor areas, such as Sub-Saharan Africa, tropical areas of Latin America, some Pacific island nations, and South and East Asia. Agriculture sector also causes greenhouse gas emissions. Climate change mitigation in agriculture will require more efficient use of fertilizer, soil conservation and better production management. Population growth in developing countries will put further pressure on agriculture for rising the food demand, land and forests for agricultural use.

1.1.1 The world production of corn

Figure 1.2 illustrates the world production of corn in 2013. United States, China and Brazil are the three most leading countries in corn production quantity in the region (FAOSTAT, 2013).

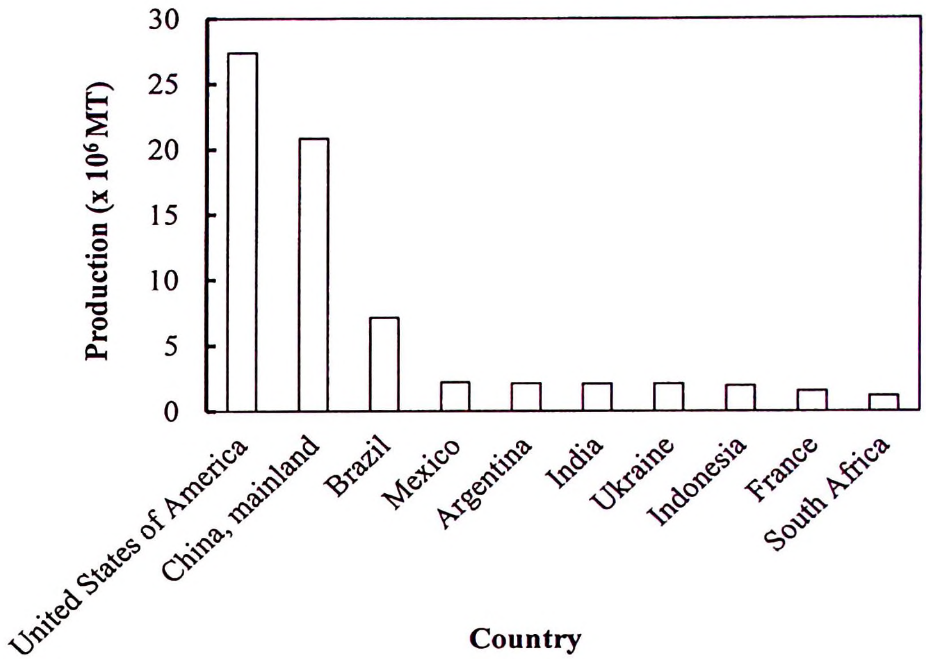


Figure 1.2: The world production of corn in 2012 (FAO, 2013).

Generally, cereal crop production in these three countries has well meaningful potential quantity which signifies sustainable availability of corn residues. Corn cob is obtained after removing the maize seeds from the cob. One of the corn cobs is made up of cellulose and lignin. The most important characteristic of corn cob products is their absorbency in which their capacity to hold up to four times their weight in fluid (Danladi & Patrick, 2013). This absorptive quality enables corn cob products to be used to absorb finishing fluids, oil and water in industrial applications and to clear up industrial or environmental spills, and it also makes the corn cob products excellent carriers for vitamins and antibiotics in animal feed or as carriers for herbicides and pesticides in lawn care products (Agrisent, 2014). Crop residues have potential to be utilized for bioenergy production. Annually approximately 204 million dry metric tons of corn residue are returned to the ground as waste by-product in corn grain production (Perlack *et al.,* 2005). Crop residues are also important as top cover on agricultural land. Residues can act as buffers to falling rain and wind shear that dislodge soil particles and cause erosion. Sun radiation, heat flux, and moisture evaporation are also affected by crop residue levels (Wilhelm *et al.,* 2004). The removal of crop residue should be balanced against the environmental impact (soil erosion), maintenance of nutrient and soil organic matter levels, and preservation of productivity levels (Wilhelm *et al.,* 2004). While corn cobs have been used on a small scale as a fuel for direct combustion in cooking and heating, their use as feedstock for large-scale energy production is a more modern concept. The large-scale use of corn cobs presents new challenges and issues to consider, production rates must be estimated such as harvesting, handling and storing methods should to be developed.

1.1.2 The generation of corn residue

Agriculture is an important part of the economy in all countries. Besides the crops itself, large quantities of residues are generated every year include corn is an example of crops that generate considerable amounts of residues. These residues constitute a major part of the total annual production of biomass residues and are an important source of energy both for domestic as well as industrial purposes. The quantity of residue produced by various crops is shown in Figure 1.3 (Shanahan, *et al.,* 2004). Using estimates from this figure, a grower could expect approximately 7,500 lbs/acre of residue from corn producing 150 bu/acre. All crop residues possess their highest quality at the time of grain harvest and decline in quality the longer they remain in the field.

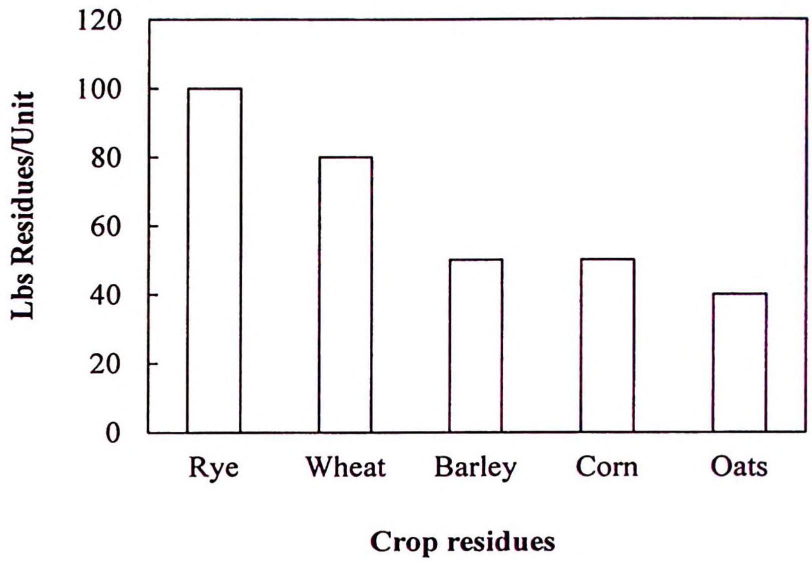


Figure 1.3: The production of residues by various crops (FAO, 2013).

1.2 Current scenario of the agricultural biomass production in Malaysia

Malaysia is located in South East Asia and spreading over three main areas, namely as Peninsular Malaysia (131,587 km^2), Sabah (73,711 km^2) and Sarawak (123,466 km^2). In year 2011, Malaysia has 328,550 total land area km^2 which is as an agricultural area with 24.0% of land area (The World Bank Group, 2014). Now agriculture has 5.27 million hectares of three main crops productions mainly oil palm, rubber and rice (Ministry Primary Industries, 2005) cultivation unlike the past, which is no longer solely a food-based contributor but plays important non-food roles, which are multifunctional; economic, social, cultural, and food security. This multi-functionality role of agriculture warrants sustainable development in the longer run. The current scenario of the Malaysian agricultural, specifically sustainable oil palm planting is deliberated against the negative claims of the world environmentalist (Pek, 2009).

Figure 1.4 represents the world production in million tonnes of major agricultural crops in Malaysia in year 2012.

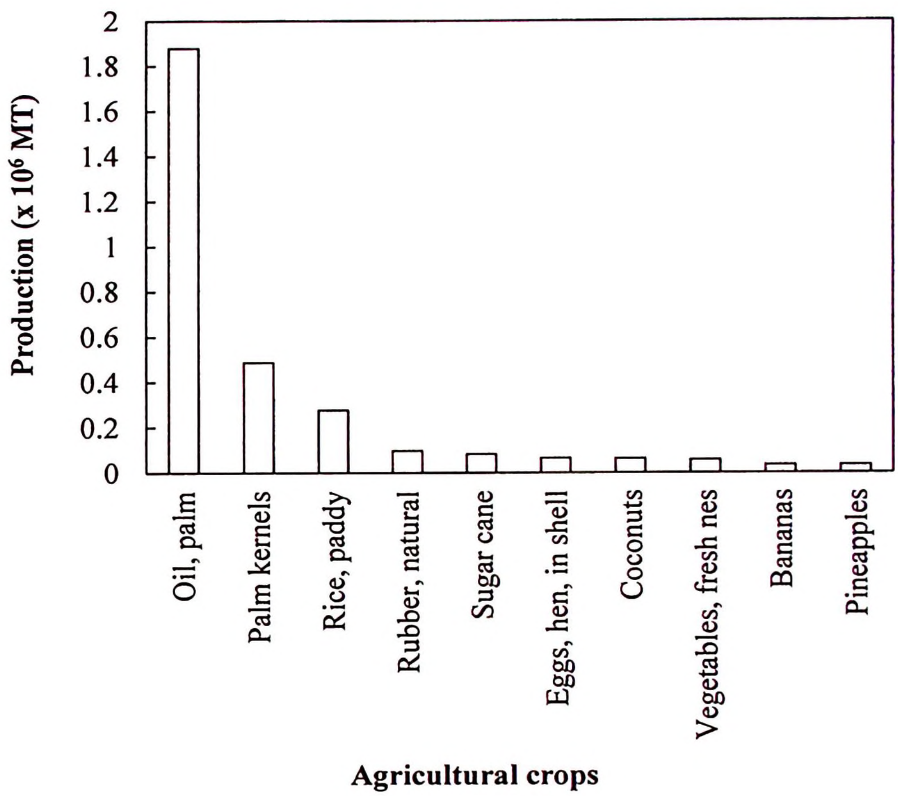


Figure 1.4: Current scenario of Malaysian production agricultural biomass in 2012 (FAO, 2013).

In Malaysia, contributions by the corn production to the agricultural sector are relatively lower. The scenario of corn production is increasing from 2007 to 2011 as stated in Figure 1.5. The primary problems with crop residues are low quality and harvesting. An advantage to using crop residues is that the cost to produce them generally is associated with the production of the grain or marketable product.

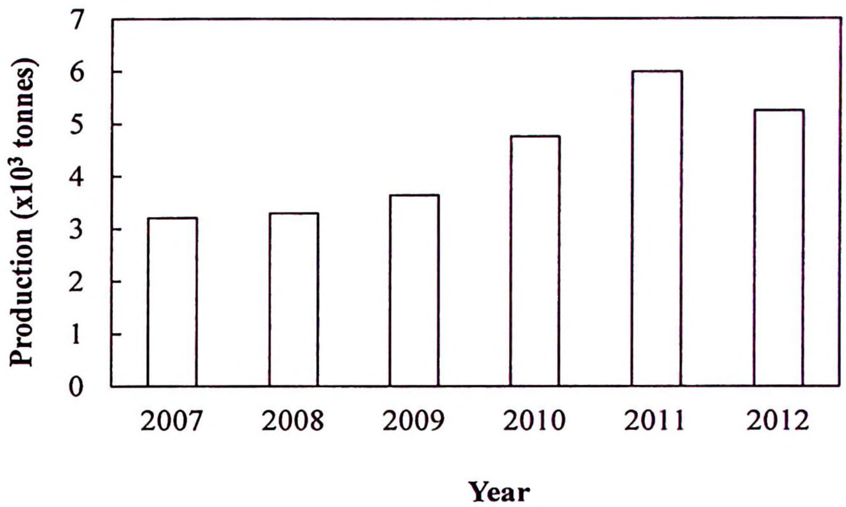


Figure 1.5: Production (tons) of corn in Malaysia (FAO, 2013).

1.3 Problem statement

Large quantity agricultural biomass are produced annually worldwide and often dumped in open environment (Chandraa *et al.,* 2012). This is because of the modernization of biomass technologies leading to more efficient biomass production and conversion is one possible direction for efficient utilization of biomass resources. The problems associated from increasing amount of weight and volume of agricultural residues, the waste disposal become one of public social and environmental concern in handling and disposal. The agricultural biomass in some cases can generate adverse effects, such as contributing to phytotoxic components of crops and soil (example given such as phenolic compound of bark, ammonia from animal manures, soluble salts, fats, weed seeds and pathogen microorganisms (Ceotto, 2005; Hern'andez-Apaolaza *et al.,* 2000; Ohno *et al.,* 2000; Peign'e & Girardin, 2004) and restricting the seed germination, destroying roots and suppressing plant growth (Mantovi *et al.*, 2003; Zmora-Nahum *et al.*, 2005) nutrient losses occur because of lixiviation to groundwater and superficial water (Hansen *et al.*, 2001; Neeteson, 2000) or emission to the atmosphere (Mei *et al.*, 2004; Su *et al.*, 2003) such as open burning.

The use of agricultural wastes as sorbents fulfils two important scopes for the protection of environment which is for the reuse of waste materials and the detoxification of wastewaters. Reuse the waste biomasses for the remediation of wastewaters by using insecticide carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate), as model pollutant. The World Health Organization (WHO) specified a standard limit of 20 and 30 µg/L for carbofuran in water portable respectively (Salman & Hameed, 2010). The departure of the carbofuran carbamate derivative pesticides has prevailed to be growing branch that protests against the invasive species which pose an enormous threat to the indigenous ecologies, and prevents against the transmission of diseases (Copper & Dobson, 2007; Jones *et al.*, 2005), thus enabling qualitative and quantitative assurance of the crops yield stability for fulfilling the pressing need of the rising food's demand (Kim *et al.*, 2008).

Carbofuran is a widely used insecticide on soybeans, rice, potatoes, fruit and vegetable crops. The use of carbofuran has become of environmental concern not only because its heavy rate of use but also because it is toxic, carcinogenic and recalcitrant. Obviously, exposure of pollutants poses a continuous health hazard, especially in using pesticides, which show a high degree of toxicity because they are designed to kill certain organisms and thus create some risk of harm. Within this context, pesticide use has raised serious concerns not only of potential effects on human health, but also about impacts on wildlife and sensitive ecosystems (Berny, 2007; Power, 2013). Furthermore, many end users have poor knowledge of the risks associated to the use of pesticides, including the essential role of the correct associated and the necessary precautions (Damalas *et al.*, 2006; Recena *et al.*, 2006; Salamah *et al.*, 2004; Yassin *et al.*, 2002). Even farmers who are well aware of harmful effects of pesticides are sometimes unable to translate this awareness into their practices (Atreya, 2007; Damalas et al, 2006; Isin & Yildirim, 2007; Zyoud *et al.*, 2010).

To purify wastewaters from these pesticide pollutants, waste water will be used in this study will deal with agricultural adsorbent due to water treatment processes known as low cost adsorption. Results from a number of extremely expensive treatment which include chemical precipitation, chemical oxidation or reduction, electrochemical treatment, membrane filtration, ion exchange, carbon sorption, and coprecipitation/sorption processes are some ineffective at low concentrations. Alternative cost effective technologies based on adsorption process by using low cost sorbents are nowadays and most frequently because of its efficiency, capabilities and applicability on a large scale (Salman & Hameed, 2010). These low cost sorbents must be abundant in nature, easily available, and above all they have to fit the worldwide request of recycling (Nurchi & Villaescusa, 2011). Certain waste products from agricultural operations may become inexpensive sorbents and the potential of some of these wastes for the removal of number pesticide pollutions has been extensively investigated.

1.4 Research objectives

The general objective of this study was to examine the feasibility of corn cob as low cost and eco-friendly biosorbent for water pollution. Specifically, the main objectives of this research are:

a) To characterize the physical and chemical properties of the prepared biosorbents.
b) To evaluate the performance of the prepared biosorbents for the adsorptive treatment of water pollutants such as carbofuran.
c) To determine the best operating condition such as the effect of time and concentration, pH and dosage.
d) To establish the adsorption modeling for the adsorption system.
e) To study the thermodynamics of the adsorption system.

1.5 Scope of study

This study explored the renewable use of corn cob as the biosorbent for removing carbofuran, a source of pollution from agricultural industries. Different modification agent and ratio on the biosorbent were examined. The functional groups allow the sorption of pollution by strong condition. Some other factors affecting the sorption process such as adsorbent dosage, initial concentration and contact time, pH and temperature were carried out. Equilibrium data were fitted by the Langmuir, Freundlich and Temkin isotherm models. The physical and chemical properties of the biosorbent were determined for the remediation of contaminated wastewater.

CHAPTER TWO

LITERATURE REVIEW

2.1 Pesticide

In general, pesticide is defined as a diverse group or mixture of chemical substances, biological agents, antimicrobials, disinfectants or devices which are intentionally applied for selective administration and attenuation against any pests including insects, plant pathogens, weeds, mollusks, birds, mammals, fish, nematodes (roundworms) and microbes that compete for the production, processing, storage, transport, or marketing of food, agricultural commodes, destroy property, or widespread of diseases (Corsini *et al.,* 2008; Dich *et al.,* 1997; Daneshvar *et al.,* 2007). Then, the Food and Agriculture Organization of the United Nations (FAO) has defined a pesticide as a substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm or otherwise interfering with the production, processing, storage, transport, or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. Also included in the FAO definition are substances intended for use as plant growth regulators, defoliants, desiccants, or agents for thinning fruit or preventing the premature fall of fruit, and substances applied to crops either before or after harvest to protect the commodity from deterioration during storage or transport (FAO, 2013).

More precisely, pesticide is featured by its unique chemical structures developed to mimic and substitute for specific molecules to the targeted pests, which present a deleterious disruption to the desired biological reactions (Gavrilescu, 2005) and among these compounds there are 22 class of pesticide classification (Table 2.1). Pesticide have immensely contributed to enhance crop productivity and to control the insect borne disease (Makehelwala *et al.*, 2012).

Table 2.1: The classification of pesticides according to their classes (Pesticide Target Interaction Database, 2012).

Class	**Pesticide name**	**Class**	**Pesticide name**
Class 1	Insecticides	Class 12	Molluscicides
Class 2	Herbicides	Class 13	Herbicide Safeners
Class 3	Fungicides	Class 14	Miscellaneous
Class 4	Acaricides	Class 15	Synergists
Class 5	Plant Growth Regulators	Class 16	Bird Repellents
Class 6	Nematicides	Class 17	Avicides
Class 7	Rodenticides	Class 18	Mammal Repellents
Class 8	Insect Attractants	Class 19	Plant Activators
Class 9	Bactericides	Class 20	Antifeedants
Class 10	Insect Repellents	Class 21	Chemosterilants
Class 11	Algicides	Class 22	Mating Disrupters

Presently, on a worldwide basis, intoxications attributed to pesticides have been estimated to be as high as 3 million cases of acute and severe poisoning annually, with many unreported cases and with some 220,000 deaths (Kumazawa & Suzuki, 2000). This situation calls for urgent attention with acceptable solution for the removal of pesticides from water sources.

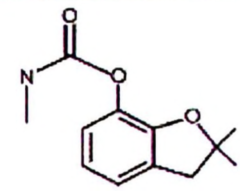
2.1.1 Carbofuran

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl-N-methyl carbamate) is a broad spectrum of systemic acaricide, insecticide, and nematicide included in the general group of the carbamate derivatives (Javier et al,. 2002). As a result of its widespread use, air, food, surface water, and underground water are contaminated with carbofuran residue and its metabolites (Tariq *et al.,* 2006), which may affect human health. The WHO specified a standard limit 30 μm/L for carbofuran in portable water respectively (Gupta *et al.,* 2006). The toxicity of pesticides and their degradation products have made these chemical substances a potential hazard for our environment (Philip *et al.,* 1991). It is widely used for the control of soil dwelling and foliar-feeding insects including wireworms, white grubs, weevils, stem borers, aphids, and several other insects (Kale *et al.,* 2001).

Several researchers have found that carbofuran is susceptible to leaching, for instance, carbofuran was classified as 'highly mobile' (McCall, *et al.,* 1980). The leaching run-off from the agricultural and forestry land; deposition from aerial applications and discharge of industrial wastewater are responsible for this water contamination (Gupta *et al.,* 2006). The maximum acceptable concentration for carbofuran in drinking water (USEPA, 1985) is 0.09 mg/L. According to EPA, there are considerable risks associated with carbofuran in food and drinking water, risks to pesticide applicators and risks to birds exposed in treated fields. Also, not all products containing carbofuran meet safety standards. This has led EPA to remind growers that carbofuran should not be used on any food crops since it was banned on December 31, 2009 (EPA, May 15, 2009). To control this hazard, the European Union (EU) has promulgated standards for drinking water at a maximum permissible level for any particular pesticide to be at 0.1 $\mu g/dm^{-3}$ and for the sum of all pesticides including their degradation products, to be at 0.5 $\mu g/dm^{-3}$ (Makehelwala *et al.*, 2012).

Carbofuran is highly toxic to animals and humans both by oral and inhalation routes and therefore, may pose a serious threat to those in contact with it in manufacturing and formulation plants or in crop fields (Gupta, 1994; Lalah & Wandiga, 1996). The ubiquitous presence of carbofuran in the environment has received a great concern not only due to its heavy usage but also due to its high oral toxicity ($LD_{50} \sim 11$ mg/kg body weight in rats) (Makehelwala *et al.*, 2012). The half-lives of carbofuran in water are a variable which ranged from 690 days at pH 5 to 7 days at pH 9 (Chapman & Cole, 1982). Due to its acute toxicity, the fate of its residue in terms of persistence and mobility is of great concern. Carbofuran is known to be a more persistent insecticide than other carbamate or organophosphorus insecticides (Jui-Hung *et al.*, 1997). Carbofuran is known to be more persistent than other carbamate or organophosphate insecticides (Jui-Hung, *et al.*, 1997). Even though carbofuran is widely used in Malaysian agriculture, to the best of the author's knowledge, no intensive research has been carried out under Malaysian conditions although there are several publications on its behaviour in tropical and temperate soils (Dowling, *et al.*, 1994; Lalah & Wandiga, 1996; Lee, *et al.*, 1990; McCall, *et al.*, 1980; Tsui & Ming, 1998; Yazgan, *et al.*, 2005). Therefore, research on the fate of carbofuran needs to be carried out in order to understand its behaviour under Malaysian environmental conditions. Table 2.2 shows the chemical structure and properties of carbofuran.

Table 2.2: The chemical and physical properties of carbofuran (Bermúdez-Couso, *et al.*, 2011).

Common Name	**Carbofuran**
Chemical Structure	
Molecular Formula	$C_{12}H_{15}NO_3$
Molar Mass (mg mol^{-1})	221.3
Molecular Weight	221
Solubility in Water (g/100g water) at 20°C	0.33 g
Log P	1.7 (Octano/Water)

2.2 Water treatment technologies

Developing researches by the invention of a wide variety of treatment technologies are available with varying degree of success to control water pollution. Some of them are coagulation (Tan *et al.*, 2000), foam flotation (Mavros *et al.*, 1994), filtration (Zouboulis *et al.*, 2002), ion exchange (Bolto *et al.*, 2002), aerobic and anaerobic treatment (Bell *et al.*, 2000; LaPara *et al.*, 2000), advanced oxidation processes (Esplugas *et al.*, 2002), solvent extraction (Lin & Juang, 2002), adsorption (Faust & Aly, 1987), electrolysis (Szpyrkowicz *et al.*, 1995), microbial reduction (Shen & Wang, 1994), and activated sludge (Pala & Tokat, 2002) with varying levels of success has accelerated a dramatic progress in the scientific community (Table 2.3).

Table 2.3: Technical advantages and drawbacks of the existing pesticides treatment technologies.

Treatment	Advantages	Drawbacks
Fenton process	Rapid decomposition of organic and inorganic pesticides. Ease handling. Ability in removing a broad range of pesticides (biodegradable and non-biodegrable). Low operational cost.	Production of residual sludge. Management can lead to accumulation of ion particles or free radicles. Require large usage of chemicals regents.
Biological Treatment	Capable for treating a wide range of pesticides which cannot be treated by chemical or membrane technologies.	Require large surface areas for implantation of treatment and biomass separation units. Limited suitability in treating stabilized pesticide carbon.
Membrane technologies	Operated without phase changes or chemical conditioning. Only low energy consumption (pressure) is needed	Subjected to the fouling effect by a wide spectrum of constituents (resulting in short lifetime of membranes and decrease of process productivity
Ion exchange treatments	Exhausted resins are regenerable. Low operational cost. Low energy consumptions.	Different resin is fabricated to selectively remove preferable types of pesticides. Improper for treating chlorinated pesticides. The presence of microorganisms can reduce the exchange capacity leading to a reduction in treated water quality.

However, most of them require substantial financial input and their use is restricted because of cost factors overriding the importance of pollution control. Of major interest, adsorption process, a surface phenomenon by which a multi-components fluid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and forms attachments via physical or chemical bonds, is recognized as the most efficient and promising fundamental approach in the wastewater treatment processes (Foo & Hameed, 2009).

Among various available water treatment technologies, adsorption process is considered better because of convenience, ease of operation, and simplicity of design (Faust & Aly, 1987). Further, this process can remove or minimize different type of pollutants and thus it has a wider applicability in water pollution control. Adsorption process has been proven one of the best water treatment technologies around the world and activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse types of pollutants from water (Bhatnagara & Sillanpääb, 2010). However, widespread use of commercial activated carbon is sometimes restricted due to its higher costs. A perusal of literature (Gupta & Ali, 2002) shows that although a large number of alternative adsorbents have been studied to replace activated carbon, the results have not been very promising. Attempts have been made to develop inexpensive adsorbents utilizing numerous agro-industrial and municipal waste materials by present a study is an effort, therefore, made in this direction to explore the potential of some industrial wastes for the removal of pesticides. Use of waste materials as low-cost adsorbents is attractive due to their contribution in the reduction of costs for waste disposal, therefore contributing to environmental protection. For this purpose, efforts were made to convert the fertilizer wastes into inexpensive and effective adsorbents.

2.3 Biosorption

Biosorption has gained important credibility in recent years because of its eco-friendly and excellent performance. Biosorption is a rapid sorption process resulting from physicochemical and ion exchange interactions occurring at the cell surface between a sorbate and live, dead, or inactive biomass. It is important to note, when using live biomass, that biodegradation may also occur concurrently with sorption phenomena and the total removal observed may consist of sorption and degradation contributions and it is difficult to distinguish the contribution of each (Javad *et al.*, 2011). Recently, various low-cost adsorbents derived from agricultural waste or natural materials, have been investigated for pollutant removal from aqueous solutions (Chang, *et al.*, 2011).

Adsorption is a mass transfer operation which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface (Kurniawan & Babel, 2003). The substance being adsorbed or removed from liquid phase is the adsorbate and the adsorbing material which is solid, liquid or gas phase onto which the adsorbate is termed the adsorbent (Mariangela *et al.*, 2012). The properties of adsorbates and adsorbents are quite specific and depend upon their constituents. The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from wastewater (Khattri & Singh, 2009).

Although certain phenomenon associated with adsorption were known in ancient times, the first quantitative studies were reported by C.W. Scheele in 1773 (Mantell, 1951) on the uptake of gases by charcoal and clays. This was followed by Lowitz' observations who used charcoal for decolourisation of tartaric acid solutions. Larvitz in 1792 and Kehl in 1793 observed similar phenomenon with vegetable and animal charcoals, respectively. However, the term 'adsorption' was proposed by Bois-Reymond but introduced into the literature by Kayser (Abrowski, 2001). Ever since then, the adsorption process has been widely used for the removal of solutes from solutions and gases from air atmosphere.

If the interaction between the solid surface and the adsorbed molecules has a physical nature, the process is called physisorption. In this case, the attraction interactions are van der Waals forces and, as they are weak the process results are reversible. Furthermore, it occurs lower or close to the critical temperature of the adsorbed substance (Bhatnagara & Sillanpääb, 2010). On the other hand, if the attraction forces between adsorbed molecules and the solid surface are due to chemical bonding, the adsorption process is called chemisorption (Bhatnagara & Sillanpääb, 2010; Mariangela *et al.,* 2012). Contrary to physisorption, chemisorption occurs only as a monolayer and, furthermore, substances chemisorbed on solid surface are hardly removed because of stronger forces at stake. Under favorable conditions, both processes can occur simultaneously or alternatively. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic.

Adsorption is the most attractive method due to its simplicity, convenience and high removal efficiency (Francesca *et al.,* 2008; Zheng *et al.,* 2009). Such factors as temperature, contact time, pH, sorbent dosage and ionic strength, presence of competing agents, sorbent and sorbate types, and sorbent specific surface area affect biosorption efficiency at various extents. Biosorption have advantages compared with conventional techniques (Volesky, 1999). Some of these are listed below:

a) Cheap: The cost of the biosorbent is low since they often are made from abundant or waste material.

b) Metal selective: The metal sorbing performance of different types of biomass can be more or less selective on different metals. This depends on various factors such as type of biomass, mixture in the solution, type of biomass preparation and physicochemical treatment.

c) Regenerative: Biosorbents can be reused, after the metal is recycled.

d) No sludge generation: No secondary problems with sludge occur with biosorption, as is the case with many other techniques, for example, precipitation.

e) Metal recovery possible: In case of metals, it can be recovered after being sorbed from the solution.

f) Competitive performance: Biosorption is capable of a performance comparable to the most similar technique, ion exchange treatment. Ion exchange is, as mentioned above, rather costly, making the low cost of biosorption a major factor. Biosorbents intended for bioremediation environmental applications are waste biomass of crops, algae, fungi, and bacteria, which are the naturally abundant.

2.4 Adsorbents

The process of adsorption implies the presence of an "adsorbent" solid that binds molecules by physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is available in large quantities, easily regenerable, and cheap. Dead and metabolically inactive cells can serve as a basis for the progress to treat and removing different classification of pesticide. They can be highly selective, cheap and efficient compare to activated carbon that used in classical methods. Activated carbon is the oldest adsorbent known and is usually prepared from coal, coconut shells, lignite, and wood, using one of the two basic activation methods: physical and chemical (Phan *et al.,* 2006). In spite of abundant uses of activated carbon, its applications are sometime restricted due to its higher cost (Bhatnagara & Sillanpääb, 2010). Therefore, this study is looking for low-cost agricultural waste adsorbents for water pollution control, where cost factors play a major role. An abundant source of potentially metal-sorbing biomass is cellulosic from agricultural wastes. Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable nature and low cost are viable option for water and wastewater remediation. Agricultural waste is a rich source for activated carbon production due to its low ash content and reasonable hardness (Ahmedna *et al.,* 2000) therefore; conversion of agricultural wastes into low-cost adsorbents is a promising alternative to solve environmental problems and also to reduce the preparation costs.

In the last several decades, various agricultural wastes have been explored as low-cost adsorbent. Some of them include the shells and/or stones of fruits like corn

(Tsai *et al.,* 2001), nuts (Ahmadpour & Do, 1997; Nguyen *et al.,* 1995; Toles *et al.,* 1998), peanuts (Wafwoyo *et al.,* 1999), olive wastes (Nyazi *et al.,* 2005), almonds (Christopher & Wayne, 2002), apricots stones (Soleimani & Kaghazchi, 2008), and cherries (Lessier *et al.,* 1994); and wastes resulting from the production of cereals such as rice (Khalil, 1996), maize (Elizalde-Gonzalez *et al.,* 2008) and as well as sugar cane bagasse (Girgis *et al.,* 1994) and coir pith (Namasivayam & Sangeetha, 2006). These agricultural waste materials have been used in their natural form or after some physical or chemical modification.

A good adsorbent should generally possess a porous structure (resulting in high surface area) and the time taken for adsorption equilibrium to be established should be as small as possible so that it can be used to remove wastes in lesser time (Linsen, 1970; Tien, 1994). Bakouri et al. in 2009 studied the potential use of natural organic substances as an ecological technique to prevent pesticide contamination of ground water resources (Bakouri & Morilloa, 2009). One of the most important characteristics of an adsorbent is the quantity of adsorbate it can accumulate which is usually calculated from the adsorption isotherms (Mariangela *et al.,* 2012).

2.4.1 Major drawbacks in the availability/supply of adsorbents

It is evident from the literature survey that various low-cost adsorbents have shown good potential for the removal of various aquatic pollutants (Faust & Aly, 1987). However, there are few issues and drawbacks on the use of low-cost adsorbents in water treatment that have been discussed (Bhatnagar & Sillanpää, 2010). Bhatnagar *et al.*, (2010) stated that some of the important issues of the drawbacks can be summarized below:

a) Selection and identification of an appropriate low-cost adsorbent is one of the key issues to achieve the maximum removal/adsorption of specific type of pollutant depending upon the adsorbent–adsorbate characteristics.

b) The conditions for the production of low-cost adsorbents after surface modification for higher uptake of pollutants need to be optimized.

c) Cost factor should not be ignored. Low production cost with higher removal efficiency of adsorbents would make the process economical and efficient.

d) Mechanistic studies need to be performed in detail to propose a correct binding mechanism of aquatic pollutants with low cost adsorbents.

e) Regeneration studies need to be performed in detail with the pollutants-laden adsorbent to recover the adsorbate as well as adsorbent. It will enhance the economic feasibility of the process.

f) The potential of low-cost adsorbents under multi-component pollutants needs to be assessed. This would make a significant impact on the potential commercial application of low-cost adsorbents to industrial systems.

g) There is scarce data available for the competitive adsorption of pollutants (metal ions adsorption in presence of phenols, dyes and other contaminants and vice-versa). Therefore, more research should be conducted in this direction.

h) It is further suggested that the research should not limit to only lab scale batch studies, but pilot-plant studies should also be conducted utilizing low-cost adsorbents to check their feasibility on commercial scale.