PREPARATION AND CHARACTERIZATION OF MICROWAVE-MODIFIED ADSORBENTS FROM *Casuarina equisetifolia* SEEDS FOR DYE ADSORPTION APPLICATION

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Thesis Submitted in Fulfillment of the Requirement for the
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Abstract of thesis presented to the Senate of Universiti Malaysia Terengganu in fulfilment of the requirement for the degree of Master of Science

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November 2016

Main Supervisor : Associate Professor Dr. Mohamad Bin Awang, Ph.D.

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School : School of Ocean Engineering

Nowadays, numerous approaches have been focused for the development of cheaper, effective and environment friendly adsorbents as alternatives to replace activated carbon and other adsorbents. In this study, raw *Casuariana equisetifolia* seeds and p-toluene sulfonic acid as well as sodium hydroxide (NaOH) treated seeds with and without microwave treatment were used as adsorbents for the malachite green (MG) and neutral red (NR) dye removal. The treated adsorbents were prepared by soaking the seeds in the p-toluene sulfonic acid and NaOH. The microwave-modified adsorbents were prepared by treating the seeds in the microwave oven with the frequency of 2.34 GHz, 800 W and 8 min irradiation time before the seeds were treated with the p-toluene sulfonic acid and NaOH. The adsorbents were characterized based on the chemical characteristic, physical characteristics and surface morphological. The batch adsorption experiments were performed for the removal of MG and NR dyes. The results reveal that microwave-acid-alkali treated *C. equisetifolia* seeds have the lowest ethanol-toluene solubility and hot water solubility that determine the quantity of extraneous materials compared raw and acid-alkali treated seeds. The lowest value of extraneous materials led to increase the active surface of adsorbent and thus promote the adsorption efficiency. Besides that, the content of lignocellulose materials of adsorbent showed higher values that can promote the binding of dyes. The FTIR spectra of microwave-acid-alkali treated seeds have high intensity of C-H stretch, C=O stretch and C-O groups at band 2924 cm^{-1}, 1701-1720 cm^{-1} and 1022-1026 cm^{-1}, respectively, which can enhance the adsorption capacity of adsorbents. Besides, the micrographs of adsorbents show that the surface of the microwave-acid-alkali treated seeds was full of cavities and cracks as compared to that of raw and acid-alkali treated seeds. Surface charge of the adsorbents show negative zeta potential values which is related to the negatively charge ion of carboxyl and phenolic OH groups that can promote the binding of cationic dyes. The equilibrium adsorption for all batch adsorption experiments was achieved within 150 min. The highest percentage of MG and NR dye removal for microwave-acid-alkali treated seeds was achieved at 1.0 g/100 mL of 200 mg/L of dye which are 95.96 and 97.24 %, respectively. Equilibrium data were best presented by Langmuir model with high correlation coefficient 0.984 to 0.999 representing the adsorption of dye was taken place at specific homogeneous sites of adsorbents. Meanwhile, for kinetic study, the adsorption process followed pseudo-second-order kinetic model with correlation coefficient between 0.7932 and 0.9980 for both dyes indicating the chemisorption has occurred between adsorbents and dye molecules.

Abstrak thesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu
sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

PENYEDIAAN DAN PENCIRIAN PENJERAP DIUBAHSUAI OLEH GELOMBANG MICRO DARI BIJI *Casuarina equisetifolia* UNTUK PENGGUNAAN PENJERAPAN PEWARNA

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Masa kini, pelbagai pendekatan telah diberi tumpuan untuk penghasilan penjerap yang murah, berkesan dan mesra alam sebagai alternatif untuk menggantikan karbon diaktifkan dan penjerap lain. Dalam kajian ini, biji *Casuariana equisetifolia* tidak dirawat dan biji dirawat dengan asid p-toluena sulfonik serta natrium hidroksida (NaOH) bersama dan tanpa rawatan gelombang mikro digunakan sebagai penjerap untuk menyingkiran hijau malachite (MG) dan merah neutral (NR). Penjerap yang dirawat disediakan dengan merendam biji di dalam asid p-toluna sulfonik dan NaOH. Penjerap diubah suai dengan gelombang mikro dirawat di dalam ketuhar gelombang mikro dengan frekuensi 2.34 GHz, 800 W dan 8 min masa penyinaran sebelum dirawat dengan asid p-toluena sulfonik dan NaOH. Pencirian penjerap dibuat berdasarkan sifat kimia, sifat fizikal dan morfologi permukaan. Penjerap dikaji dalam eksperimen penjerapan kelompok untuk menyingkirkan pewarna MG dan NR. Keputusan menunjukkan biji *C. equisetifolia* dirawat gelombang mikro-asid-alkali mempunyai kelarutan etanol-toluena dan air panas terendah yang menunjukkan kuantiti bahan luaran berbanding dengan biji tidak dirawat dan dirawat oleh asid-alkali. Nilai kandungan bahan luaran yang rendah dapat meningkatkan permukaan aktif pada penjerap dan seterusnya meningkatkan kecekapan penjerapan. Selain itu, bahan lignoselulosa bagi penjerap menunjukkan nilai tinggi dapat membantu ikatan pewarna. Spektrum FTIR bagi biji dirawat gelombang mikro-asid-alkali mempunyai intensiti yang lebih tinggi pada regangan C-H , ikatan C=O dan kumpulan C-O pada lingkaran 2924 cm^{-1}, 1701-1720 cm^{-1} dan 1022-1026 cm^{-1} yang boleh meningkatkan kapasiti penjerapan. Selain itu, mikrograf penjerap menunjukkan permukaan biji dirawat mikro-asid-alkali mempunyai rongga dan keretakan berbanding biji tidak dirawat dan dirawat asid-alkali. Cas permukaan penjerap menunjukkan nilai negatif bagi potensi zeta yang berkaitan ion bercas negatif pada kumpulan OH karboksil dan fenolik yang boleh menggalakkan mengikatan pewarna kationik. Keseimbangan penjerapan bagi semua eksperimen penjerapan kelompok telah dicapai dalam tempoh 150 minit. Peratusan penyingkiran tertinggi pewarna MG dan NR untuk biji dirawat mikro-asid-alkali adalah pada 1.0 g/100 mL bagi 200 mg/L kepekatan iaitu masing-masing 95.96 dan 97.24%. Data keseimbangan yang terbaik ditunjukkan oleh model Langmuir dengan pekali korelasi yang tinggi iaitu 0.984-0.999 menunjukkan penjerapan pewarna berlaku pada laman homogen tertentu pada penjerap. Sementara itu, untuk kajian kinetik, proses penjerapan mengikuti model kinetik pseudo-kedua dengan pekali korelasi antara 0.7932 dan 0.9980 untuk kedua-dua pewarna yang menunjukkan penjerapan kimia telah berlaku antara penjerap dan molekul pewarna.

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In the name of ALLAH the Most Gracious and Most Merciful

Praise and glory be to Allah S.W.T. for granted me the will to going through the toughest times, also for the wisdom and determination to complete this research.

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APPROVAL

I certify that an Examination Committee has met on 22nd November 2016 to conduct the final examination of Anis Ayuni binti Aman Zuki, on her Master of Science thesis entitiled “Preparation and Characterization of Microwave-Modified Adsorbents from *Casuariana equisetifolia* seeds for Dye Adsorption Application” in accordance with the regulations approved by the Senate of Universiti Malaysia Terengganu. The Committee recommends that the candidate be awarded the relevant degree. The members of the Examination Committee are as follows:

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DECLARATION

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

ANIS AYUNI BINTI AMAN ZUKI

Date:

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LIST OF ABBREVIATIONS

AC	-	Activated carbon
AMMRF	-	Australian Microscopy and Microanalysis Research Facility
BET	-	Brunauer-Emmett-Teller
BOD	-	Biochemical oxygen demand
COD	-	Chemical oxygen demand
EKA	-	Electrokinetic analyser
FRIM	-	Forest Research Institute Malaysia
FTIR	-	Fourier Transform Infrared
IR	-	Infrared
IUPAC	-	International Union of Pure and Applied Chemistry
MG	-	Malachite green
MT	-	Million tonnes
NF	-	Nanofiltration
NR	-	Neutral red
RO	-	Reverse osmosis
SEM	-	Scanning electron microscopy
TAPPI	-	Technical Association of the Pulp and Paper Industry
TDS	-	Total dissolved solid
UMT	-	Universiti Malaysia Terengganu
UV	-	Ultraviolet

LIST OF SYMBOLS

λ_{max} - Maximum wavelength (nm)

C_0 - Concentration of dye at initial (mg/L)

C_e - Concentration of dye at equilibrium (mg/L)

q_e - Amount of dye adsorbed/adsorption capacity (mg/g)

q_{max} - Maximum adsorption capacity (mg/g)

q_t - Amount of dye adsorbed at any time (mg/g)

m - Mass of adsorbent (g)

V - Volume of dye solution (L)

K_L - Langmuir constant (L/mg)

K_f - Freundlich constant

R_L - Separation factor/equilibrium parameter

n - Intensity of the adsorption

t - Time (min)

k_1 - First-order rate constant (min^{-1})

k_2 - Second-order rate constant (g/mg.min)

h - Initial sorption rate (mg/g.min)

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CHAPTER 1

INTRODUCTION

This chapter provides an outline of the study which highlights the research background as well as problem statements, research aim and objectives, research significances and research scopes. It also focuses on the general ideas of the preparation and production of the adsorbent from *Casuarina equisetifolia* seeds.

1.1 Background of the Research

Water is one of the main natural resources that plays important roles for living systems on Earth. The most widely recognized wellsprings of water include rivers, reservoirs, lakes, and groundwater. Each year, trillions litres of fresh water, together with huge amounts of chemicals have been consumed by the global industries. The wastewater containing toxic substances from the industry is then discharged into stream, ultimately end up into the sea, where it spreads around the earth (Sloan *et al.*, 2013).

The dye-based industries have brought in a public health threat because of the contamination of a huge range of chemical contents and dyes. The main release of contamination from industrial occurs during dyeing and finishing processes, and it is discharged by the manufacturer into streams or river. The discharged wastewater is not generally biodegradable and regularly pose serious environmental and health threats to the local community. In textile dyeing and finishing process, there are a range of generally organic compounds of complex structures consumed. The discharge of coloured wastewater from textile industries, newspapers industries and printing industries into rivers or natural streams has caused many harmful effects to human, aquatic ecosystem and environment (Kaushik *et al.*, 2009).

There are numerous chemical, physical and biological techniques that have been practiced by the dye-based industries for the dye removal in wastewater (Ghoreishi and Haghighi, 2003). In the removal of dye from wastewater, there are several benefits and weaknesses of different techniques. Adsorption is the best technique that can be utilized to remove various kinds of colouring materials among of the physicochemical techniques (Sulaymon *et al.*, 2009; Liau, 2010). Adsorption has found to be most commonly used to other techniques because of the flexibility, simplicity of design, initial cost, and insensitivity to toxic pollutant and ease of operation. Adsorption also does not produce harmful substances. There are several factors that influence the adsorption efficiency such as adsorbate-adsorbent interaction, adsorbent surface area, adsorbent to adsorbate ratio, adsorbent particle size, temperature, pH and contact time (Crini, 2006; Allen and Koumanova, 2005).

As indicated by US Environmental Protection Agency, the best accessible control technologies is activated carbon adsorption. Consequently, the uses of activated carbon is limited because of their high cost. Lately, various strategies have been considered for the improvement of cheaper and operative adsorbents in order to avoid the high cost treatment of dye wastewater (Crini, 2006). The waste containing lignocelluloses from agriculture and forestry is a kind of reproducible resources, which is a high-grade raw material for preparing adsorbent due to its high carbon contents. The agricultural waste can be used to prepare adsorbents are mainly from the shells or stone, stalk or straw, bark, seeds and bagasse (Tang *et al*., 2012).

In this research, the adsorption properties of *C. equisetifolia* seeds were studied. The *C. equisetifolia* seeds were used as an adsorbent due to its vast availability since the seeds are abundant in nature, plus the fact that they are non-toxic, environmental friendly, biodegradable and relatively low cost for raw materials. *C. equisetifolia* is a group of species in the family Casuarinaceae, local to Australia, southeastern Asia and islands of the western Pacific Ocean (Ogunwade *et al.*, 2011). Its wood can be used for various purposes such as for car pole and veranda construction. The plant is recognised to store tannins and proline as well as being a nitrogen fixing plants (Tani and Sasakawa, 2006). *C. equisetifolia* plant is highly valued as an important species for erosion control and has ability as an excellent windbreak (Joker, 2000).

The *C. equisetifolia* seeds were activated by microwave radiation prior to the treatment using green chemical *p*-toluene sulfonic acid monohydrate and sodium hydroxide (NaOH) in aqueous solution. The *p*-toluene sulfonic acid monohydrate was considered as green chemical because the use of *p*-toluene sulfonic acid can minimal the formation of undesired products from side reaction and minimal generation of environmentally unfriendly waste (Mahindaratne and Wimalasena, 1997). Besides that, NaOH used in this study was at low concentration that would not result in effects on aquatic organisms because NaOH would be neutralised by others substances in water and the pH would not increase. The microwave radiation was used for activation of seeds because it gave the effects to the surface morphological structures of the seeds. Meanwhile, the acid and alkali treatment were used in order to oxidize porous carbon surface, remove mineral elements such as silica and produce positive surface charge on adsorbent that can enhance the adsorption performance of the seeds.

1.2 Statement of the Problem

Textile industry plays important role in the economic growth in Malaysia. The textile based products industry was the ninth biggest export earner with RM10.3 billion, contributing to 1.4 percent of Malaysia’s total exports of manufacturing goods in year 2013 (Mida, 2015). High concentration of dyes in wastewater that have been discharged from textile industries into stream or river gives harmful effects to human, aquatic ecosystem and environment. The discharge of dyes into the stream or river is undesirable because of their colours as well as the characteristics of breakdown results of the dyes which are mutagenic, carcinogenic, and toxic (Yagub *et al*., 2014).

The dye-containing wastewater from the textile industry is a main sources of severe pollution problems around the world. According to Sen *et al*. (2011), over 10, 000 dyes with a total yearly production over 700,000 metric tonnes worldwide are commercially available. From the values, the lost dyestuff in the industrial runoffs are about 5 to 10 percent. Almost 100 tonnes from more than 10,000 tonnes of total dye utilization in the textile industry worldwide are released into rivers (Yagub *et al.*, 2012). Meanwhile, total textile dye lost during dyeing process are from 10 to 25% and 2 to 20% of the dyes are directly discharged as aqueous effluents into streams (Zaharia *et al.*, 2009). Nowadays, the textile industries face problems to save release of wastewater because of the intricate nature of dye and difficulty to treat by conventional techniques (Selvakumar *et al.*, 2013).

Textile wastewater consists of many contaminants and pollutants including acids, soluble bases, dyes, pigments, dispersants, phthalates, heavy metals, natural chlorines, salt and many more. The pH, Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) levels of rivers and streams water are altered due to the release of these hazardous materials. Since an environmental conflict and government regulation needs textile wastewater to be treated, hence there is a requirement to have an operative method that can remove these dyes effectively (Salleh *et al.*, 2011).

There are chemical, physical and biological techniques have been broadly utilized for the treatment of dye-based wastewater. The techniques include adsorption, coagulation/ flocculation, membrane filtration, ozonation, advances oxidation and liquid-liquid extraction (Vimonses *et al.*, 2009; Yao *et al.*, 2009; Abd El-Latif *et al.*, 2010; Ghaedi *et al.*, 2011). However, those techniques have limitations. The elimination of dyes along with organic materials in a commercial way remains a serious issues despite the fact that numerous approaches has been established with adsorption method. As compared to other techniques, adsorption is an operative separation technique. Besides that, nowadays, it is thought to be incredible for water treatment as far as the simple design, initial cost and ease of operation as well as obtuse to toxic substance (Mohammad *et al*,. 2010; El-Latif *et al.*, 2010).

Activated carbon (AC) has been turned up to become an operative and commonly utilized adsorbent for the removal of organic and inorganic contaminations that dissolved in aqueous solution or gaseous environment (Derbyshire, 2001). However, the use of activated carbon was limited due to their high cost (Srivastava *et al.*, 2007). The AC is quite expensive, non-selective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. The application of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications (Streat *et al*., 1995). Therefore, there are numerous demands of the other adsorbents made up of reasonable materials and locally accessible such that the adsorption technique will turn out to be financially practical.

There are numerous current research that focused on the need to substitute commercial activated carbon as the cost effective, but potential adsorbent. Many researchers have reported the feasibility of using various low cost adsorbents derived from natural materials, industrial solid wastes, agricultural by-products and biosorbents as precursors. Among those materials, researchers successfully proved that the adsorbent from agro-based has capacity to be good and effective adsorbents for dye removal such as the adsorbent from cashew nut shell (Subramaniam and Kumar Ponnusamy, 2015), leaf powder (Chowdhury *et al.*, 2011), pine cone (Dawood and Sen, 2012) and barley straw (Ibrahim *et al*., 2010). The adsorption capacity of those agro-based adsorbent were in the range of 20 to 400 mg/g which are almost similar to the conventional available activated carbon (Crini, 2006).

Different physical, chemical or biological treatments were applied to the raw biomass adsorbents for improving their adsorption capacity which were also reported by the investigators (Rehman *et al*., 2012). Among of these three treatments, chemical treatment has been more commonly employed to increase the adsorption and hence removal capacity of adsorbents (Gautam *et al*., 2014). Recently, acidic treated rice straw was prepared to produce potential adsorbents for the removal of dyes from aqueous solutions (Gong *et al*., 2007). Ebrahimian Pirbazari *et al*. (2014) have developed adsorbent from alkali treated Foumanat tea waste for methylene blue adsorption. Meanwhile, microwave treatment was commonly applied for the activation of adsorbent in order to alter the surface morphology of adsorbents (Zhang *et al*., 2013; Njoku *et al*., 2013). However, the acidic treatment of adsorbent may decrease BET surface area and pore volume of adsorbent, meanwhile, alkaline treatment may sometimes decrease the uptake of metal ions. Therefore, the combination of acid, alkali and microwave treatment for activation of adsorbent may enhance the effectiveness of *C. equisetifolia* seeds for dye removal.

1.3 Aim and Objectives of the Research

The aim of this research is to study the potential of *Casuarina equisetifolia* seeds as an adsorbent for dye removal.

The objectives of this research are:

i) To identify the effects of the microwave-acid-alkali treatment on chemical, physical and morphological properties of adsorbent prepared from *C. equisetifolia* seeds.

ii) To study the adsorption performance of dyes on untreated and treated adsorbent from *C. equisetifolia* seeds.

iii) To study the equilibrium adsorption of dyes on adsorbent from *C. equisetifolia* seeds based on Langmuir and Freundlich isotherm models

1.4 Significance of the Research

The removal of dyes from industrial wastewater is importance in numerous countries worldwide for both water reuse and environmental concerns (Choy *et al.*, 1999). Nowadays, the accessible water treatment technologies for the removal of dyes comprise membrane filtration, chemical precipitation, electrochemical processes, ion exchange and adsorption. Adsorption is a standout amongst the most important techniques for wastewater treatment and offers a few points of interest particularly in the removal of various kinds of dyeing materials (Ghoreishi and Haghighi, 2003; Mittal *et al.*, 2006).

Until now, activated carbon is the most utilized adsorbent for dye removal in view of its high adsorption capabilities for a broad range of natural compound. However, the preparation and regeneration costs of activated carbon have encouraged the application of alternative materials. In order to reduce the high charge treatment of dye wastewater, various approaches have been examined for the advancement of effective as well as cheap adsorbents. In general, adsorbent can be presumed to be economical on the off chance that it require small handling as well as abundant in nature or as by-product or waste material from another manufacturing (Bailey *et al.*, 1999). Therefore, the development of cheaper and effective adsorbent was required to substitute the activated carbon.

This research explores the feasibility and viability of using *C. equisetifolia* seeds as an adsorbent for the removal of dyes. *C. equisetifolia* are mainly grows along the sandy coasts and they are easily found along the Terengganu beach. The unemployed *C. equisetifolia* seeds were used in this research due to its abundance availability at low cost for raw materials as well as the seeds are non-toxic, environmental friendly and biodegradable since they are from plants-based. Microwave treatment was used in this study to activate the surface of the adsorbent from *C. equisetifolia* seeds. Microwave treatment was a conceivable approach to resolve the issues of the thermal gradient and high cost as well as reducing time preparation of adsorbent. The utilization of microwave radiation in the preparation of adsorbent can increase sintering temperature, shorten preparing time and thus offer higher energy saving (Thakur *et al*., 2007). Therefore, this research was conducted in order to develop low cost adsorbent from plant-based and the treatment methods of adsorbents.

1.5 Scope of the Research

The study focused on the characterizing the chemical composition, surface functional group, surface charge and morphology of the *C. equisetifolia* seeds before and after treatment with microwave and acid-alkali treatment as well as the determination of the effect of contact time, initial dye concentration and adsorbent dosage toward the adsorption of dye onto *C. equisetifolia* seeds. The study also focused on identifying the adsorption isotherms of the dyes onto *C. equisetifolia* seeds.

To achieve the objectives of the research, the scopes of the work were identified as follows:

i) The study focused on the use of *C. equisetifolia* seeds as adsorbents in dye removal. *C. equisetifolia* seeds were collected from Pantai Teluk Ketapang, Kuala Terengganu in Terengganu, Malaysia.

ii) The microwave-acid alkali treated *C. equisetifolia* seeds were activated by using microwave oven having a frequency of 2.45 GHz and 800 W for 8 minutes irradiation. The acid-alkali treated *C. equisetifolia* seeds were treated by using 1M of *p*-toluene sulfonic acid monohydrate and 0.1M of NaOH.

iii) The study was conducted based on a batch adsorption study using Malachite Green and Neutral Red dyes.

iv) The characterizations of adsorbent in this research were performed by Fourier Transform Infrared Spectroscopy (FTIR), Electrokinetic analyser (EKA), Scanning Electron Microscopy (SEM) and UV-Visible Spectrophotometer.

v) The studied parameters tested were included contact time (0 – 240 min), initial dye concentration (200 – 400 mg/L) and dosage of adsorbent (0.2 – 1.0 g) for the uptake of dye by *C. equisetifolia* seeds.

vi) All experiments were conducted at the laboratory in Universiti Malaysia Terengganu (UMT) and Forest Research Institute Malaysia (FRIM).

CHAPTER 2

LITERATURE REVIEW

This chapter discovers the relevant literature to understand the details and relates to the research. It also provides the information related to the recent studies about the adsorption by some other researchers. This chapter also explains the concepts and ideas that can be used in order to achieve the aim and objectives of this research.

2.1 *Casuarina equisetifolia* plants

C. equisetifolia plants usually grow at the narrow strip near to the sandy coasts and it can be found on sand banks and in sands nearby estuaries. This plant also can be found behind fore-dunes as well as slopes near the sea. The plants normally situated at the main edge of sandbank vegetation, subject to salt splash and immersion with seawater at extremely high waves (Awale & Phillott, 2014). *C. equisetifolia* plants are native plants from Australia eastbound to Melanesia and westward to seaside of Southeast Asia (Whistler & Elevitch, 2006). *C. equisetifolia* plants might be the main woody species grow over a ground front of sandbank grasses and salt-tolerant broadleaved herbs. The plant is also called as the Indo-Pacific strand vegetation since the plant can likewise be part of a wealthier association of shrubs and trees (Orwa *et al.*, 2009).

C. equisetifolia plants typically have a solitary straight, rough-barked trunk and an open, uneven crown of branches. The plants have pine-like appearance due to its little, round, cone-like fruits and long, wispy, grayish green needle-like branchlets. The leaves of the plants are decreased to minor scales up it whorls of 6 to 8 leaves per whorl at nodes along the length of the branchlets. *C. equisetifolia* also have fine and non-descripts brown flower. *C. equisetifolia* seeds are winged and can be dispersed by water and wind. The solitary seed measures 6 to 8 mm long is pale brown and possesses a membranous wing as shown in Figure 2.1 (Pernas *et al.*, 2013). *C. equisetifolia* plants are usefull plant that used in timber production, landscaping, material for protecting, fuel and as wind breaker at coastal area (Awale & Phillott, 2014; Whistler & Elevitch, 2006).

Figure 2.1: *C. equisetifolia* seeds
(Source: Pernas *et al.*, 2013)

2.2 Dye Removal Treatment

Numerous industries uses dyes to colour their products such as dyestuffs, textile, newspapers and plastics industries. Consequently, they produce coloured wastewater contains contaminants including dyes. Due to the toxicity and carcinogenic nature of dyes from the industries wastes, the removal of dyes is important before it is released.

Nowadays, there are several treatment for elimination of dyes from industrial wastewater has been explored. The technologies such as chemical, biological and adsorption have their own advantages and disadvantages in the treating of dyes in industrial wastewater.

2.2.1 Chemical Treatment

Wastewater containing dyes can be treated by using several techniques including coagulation or flocculation combined with flotation and filtration, precipitation-flocculation with Fe(II)/$Ca(OH)_2$, electro-kinetic coagulation, electro-flotation, conventional oxidation methods by oxidizing agents, irradiation or electrochemical processes (Kurniawan *et al.*, 2006). All of these techniques are usually costly and in spite of the fact that the dyes are removed, accumulation of concentrated sludge generates a disposal issue. Moreover, there is a probability that a secondary pollution issue emerges as a result of the excessive chemical use.

Due to the simplicity of application and short reaction times involved, oxidation can be the most generally used technique of decolourization by chemical ways (Robinson *et al.*, 2001). According to Gupta and Suhas (2009), oxidation can be upgraded by controlling the pH and utilizing the catalysts in the breakdown of metal complex dye such as iron, copper, nickel and chromium. These techniques are modern and the metals have a catalytic influence that can rise decolourization. The principle oxidizing agent is commonly hydrogen peroxide (H_2O_2), this agent should be enacted by a few ways, for instance, ultraviolet (UV) light.

Currently, there are advanced oxidation processes have been used for the pollution degradation since the generation of very powerful oxidizing agents, for example hydroxyl radicals, chlorine, ozone, Fenton's reagent, ultraviolet with peroxide and ultraviolet with ozone. The techniques are used in the removal of dye because the modern dyes are resistant to mild oxidation conditions (Munter, 2001). One of the new advanced oxidation processes is photocatalytic degradation. This method are widely used in the mineralization the dye compounds. There are numerous studies in the removal of dye by using photocatalytic degradation process. Ameta *et al.,* (2012) have studied the degradation of methylene blue by photocatalytic process using calcium oxide. The results also showed an accomplishment to the removal COD. They have concluded that the photocatalytic is very operative technology for the degradation of methylene blue. Despite the fact that the photocatalytic process is proficient for the wastewater, the process is immoderate and commercial unfriendly. The utilization of chemical reagents and high electrical energy demand are regular issues faced (Babel & Kurniawan, 2004).

In addition, the chemical treatments are additive processes. As a result, there is generally a net increment in the dissolved constituents in the wastewater. For example, where chemical are added to enhance the removal efficiency of particulate sedimentation, the total dissolved solids (TDS) concentration of the wastewater is always increased. This additive aspect is in contrast to the physical unit operation and biological unit processes, which may be described as being subtractive, in that sense, wastewater constituent are removed from the wastewater. A critical weakness of the chemical treatment is the handling, treatment and disposal of the extensive volumes of sludge that are delivers (Gupta *et al.*, 2012).

2.2.2 Biological Treatment

The commonly reasonable alternatives for dye wastewater compared to physical and chemical treatment is biological treatment (Crini, 2006). Biological treatment in the wastewater technologies is cheaper treatment compared to other methods. Biological treatment investment cost is 5 to 20 times less and operating expenses are 3 to 10 times lower than chemical treatment (Karthik *et al.*, 2014). There are several treatments generally used to treat the industrial effluents, for example, microbial decolourization, fungal decolourization, bioremediation systems and adsorption by microbial biomass. These treatment are mostly used because many microorganisms, such as bacteria, yeast, algae and fungi can degrade and accumulate different dyes in wastewater (Fu & Viraraghavan, 2001; Robinson *et al.*, 2001).

The overall purposes of biological treatment are to change or oxidize dissolves and particulate biodegradable constituents into satisfactory finished products and to collect and incorporates suspended and non-settleable colloidal solid into a biological floc or biofilm. Besides that, biological treatment are used to change or evacuate nutrients for example nitrogen and phosphorus. The treatment also used to expel particular trace organic constituents and compounds. For industrial wastewater, the purpose of biological treatment is to expel or diminish the concentration of organic and inorganic compounds. The pre-treatment might be required before industrial wastewater can be released to a municipal collection system since a few constituents and compounds originate in industrial wastewater are toxic to microorganisms which can destroy the ecosystem (Metcalf & Eddy, 2003).

Recent study from Selvam *et al.*, (2012) on biological treatment of Azo dyes and textile industry waste by freshly disengaged white rot fungi *Schizophyllum commune* and *Lenzites eximia*. The batch and continuous mode for the removal of textile dye effluent by *Schizophyllum commune* was observed at 76.15% and 55.92 respectively on fifth day. Meanwhile, the removal of textile dye by *Lenzites eximia* in the batch and continuous mode on fifth day was showed at 75.23% and 54.60% respectively. The study showed that *Schizophyllum commune* and *Lenzites eximia* is used proficiently in removal of textile dyes. Another study have been considered on the degradation of textile dye reactive navy – blue Rx (Reactive blue–59) by an isolated *Actinomycete Streptomyces krainskii* SUK – 5 (Mane *et al.*, 2008). The findings of the study showed the isolated *Actinomycete*, *Streptomyces krainskii*, SUK -5 decolorized and degraded textile dye Reactive blue–59.

However, there are several disadvantage of biological treatment in the removal of dye. Biological treatment needs an extensive land area. Besides that, the treatment is compelled by affectability to diurnal variety as well as toxicity of a few chemicals and fewer adaptability in design and operation. Besides, Robinson *et al*,. (2001) stated that biological treatment is unequipped for acquiring acceptable colour disposal with recent conventional biodegradation. Furthermore, Ravi Kumar *et al.*, (1998) indicated that though numerous organic molecules are degraded, many organic molecules are intractable because of their complex chemical structure and synthetic organic origin.

2.2.3 Physical Treatment

The physical treatment in wastewater technologies includes the removal of substances by utilization of certainly occurring forces, for example, electrical attraction, gravity and van der Waal forces. The methods commonly used in physical treatment are sedimentation, membrane filtration and adsorption techniques. As indicated by National Drinking Water Clearinghouse Fact Sheet, membrane filtration methods are widely used in the elimination of bacteria and other microorganisms, particulate materials, and natural organic materials that can transmit colour, tastes and odours to the water. In the membrane filtration, the method includes nanofiltration, reverse osmosis and electro dialysis. Reverse osmosis processes in membrane filtration can eliminate hardness, colour and many kinds of bacteria and viruses, and organic contaminants simultaneously.

Numerous researches have investigated the utilization of membrane filtration on the removal of dyes. Abid *et al.*, (2012) explored the elimination of acid red, reactive black and reactive blue dyes by membrane technologies reverse osmosis (RO) and nanofiltration (NF). NF membranes demonstrated the final red, black and blue dye removal were at 93.77%, 95.77% and 97%, respectively. The results indicated that the application of NF in the dye removal from wastewater was effective with high efficiency compared to the current biological methods. However, membrane filtration possesses a few weaknesses such as high initial capital costs, high maintenance and operational costs, and membrane fouling as well as limited flow-rates (Gautam *et al.*, 2014; Qin *et al.*, 2002).

2.2.4 Adsorption

A method of aggregating substances in a solution on an appropriate interface is called adsorption process. The process includes the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. The adsorption process forms a film of the adsorbate on the surface of the adsorbent. The adsorbate is the substance that being expelled from the liquid phase at the interface, meanwhile, the adsorbent is the solid, liquid or gas phase onto which adsorbates aggregates or accumulates (Dąbrowski, 2001).

The adsorption process can result either from physical adsorption or physisorption named universal van der Waals interactions, or from chemical adsorption or chemisorption. A reversible process that occurs at the temperature near or lower to the critical temperature of an adsorbed substance is called physical adsorption. Critical temperature is the temperature of adsorbate in its critical state which is above this temperature, the adsorbate cannot be separated by pressure alone. It is drawn that the heat of physical adsorption is close to that of condensation and it goes along with a decline in entropy and free energy of the adsorption system. Thus, the process is called exothermic. Meanwhile, chemisorption happens only at a monolayer. It occurs typically at higher temperature compared to critical temperature. Chemisorption is a particular process that can displace on some solid surfaces for a given mass (Allen, 2005).

Figure 2.2 illustrates the adsorption process. The process occurs in several steps which are bulk solution transport, film diffusion transport, pore transport and adsorption. The step in which the movement of the organic material to be adsorbed through the bulk liquid to the boundary layer of fixed film or liquid surrounding the adsorbent is called bulk solution transport. This step normally by advection and dispersion of carbon contactors. The advection is the transport of the adsorbed substances through carbon contractors and the dispersion is the distribution of adsorbed substances to the carbon contractors. Next, the transportation of the material by diffusion through the stagnant liquid film to the entrance of the pores of the adsorbent. This step is named film diffusion transport. Furthermore, pore transport involves the movement of the material to be adsorbed by an arrangement of molecular diffusion through the pore liquid or by diffusion along the surface of the adsorbent via the pores. Then, the adsorption takes place when the materials to be adsorbed are attached to an accessible adsorption site (Snoeyink & Summers, 1999).

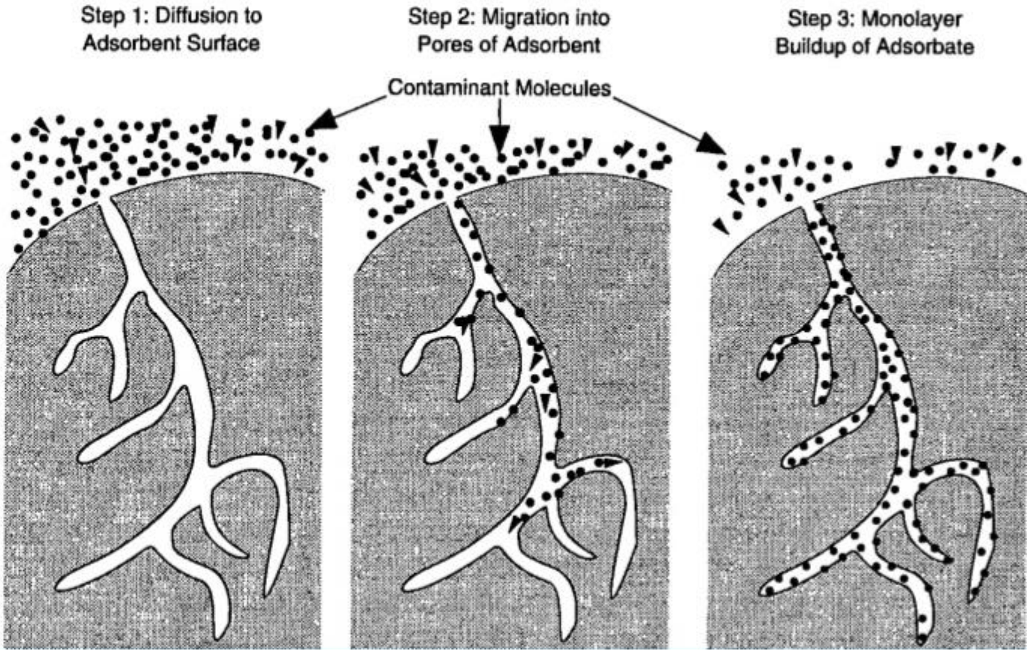


Figure 2.2: The mechanism of adsorption

(Source: Snoeyink and Summer, 1999)

In the water and wastewater treatment, adsorption is one of the most widely utilized techniques which offers several advantages especially in the elimination of various kinds of dyeing materials. Adsorption has been found to be common technique due to the initial cost, flexibility and ease of design, simplicity of operation and insensitivity to toxic pollutants (Crini, 2006). In the adsorption treatment, solid sorbents or adsorbents are commonly used to eliminate the chemical pollutants from water.

Most of the solid adsorbents own a complex porous structure in which comprises of pores with various sizes and shapes. Total porosity is typically ordered into 3 groups. As indicated by the IUPAC recommendation, the pores with a width not more than 2 nm is characterized as micropores. Meanwhile, mesopores are pores with a width between 2 and 50 nm, and macropores characterize pores with a width larger than 50 nm. Figure 2.3 shows the pores division of an adsorbent. In the adsorption process, the roles of pores mostly rely on their sizes. The pore volume on the other hand, is the fundamental controlling factor of the adsorption in micropores which is basically a pore-filling process (Dabrowski, 2001).

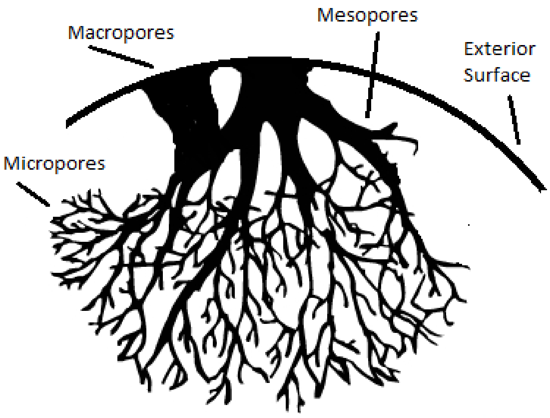


Figure 2.3: The pores of an adsorbent

(Source: Dabrowski, 2001)

Meanwhile, in the case of mesopores whose walls are formed by a great number of adsorbent atoms or molecules, the boundary of interphase has a distinct physical meaning. It means that a physical meaning also found at the adsorbent surface area. In the case of macropores, the action of the adsorption forces does not happen all through their void volume yet rather at the adjacent separation from their walls. Therefore, the monolayer and multilayer adsorption take place successively on the surface of mesopores and their final fill proceeds according to the mechanism of capillary adsorbate condensation.

There are several type of industrial adsorbents used as listed in Table 2.1. The standard types of adsorbents involve activated carbon, synthetic carbon, synthetic polymeric and silica-based adsorbents. In wastewater adsorption, silica-based and synthetic polymeric adsorbents are not regularly utilized because of their high cost. The most widely used adsorbents in advanced wastewater treatment applications is the activated carbon. In wastewater treatment, the adsorption by activated carbon is commonly expected to be an improving technique for water that has previously receives normal biological treatment. The activated carbon in the wastewater treatment is utilized to eliminate a portion of the remaining dissolved organic matter (Naseem, 2012).

Table 2.1: Basic categories of industrial adsorbent (Dabrowski, 2001)

Mineral adsorbents	Carbon adsorbents	Other adsorbents
Silica gel	Active carbons	Composite adsorbents:
Activated alumina	Activated carbon fibres	(complex mineral-carbons,
Ziolites	Mesocarbon microbeads	X-elutrilithe; X = Zn, Ca)
Clay materials	Molecular carbon sieves	Synthetic polymers
Oxides of metals	Fullerenes	Mixed adsorbents
Hyroxides of metals	Heterofullerenes	
Pillared clays	Carbonaceous nanomaterials	
Porous clay hetero-structures (PCHs)		
Inorganic nanomaterials		

Nowadays, activated carbon are widely used adsorbents due to their effectiveness as well as reliable physiochemical processes for wastewater treatment of dyes. They are known for their large surface area, high degree of surface reactivity, variable surface chemical composition as well as high adsorption capacity (Gómez *et al.*, 2007; Tseng & Tseng, 2005). However, activated carbon tend to be expensive materials in many countries because of their high preparation and regeneration cost. This factor has encouraged to development of cheap and effective substitutes for the activated carbon (Dias *et al.*, 2007).

Among numerous adsorbents, naturally available plant biomass and plant waste materials were commonly used as low cost adsorbents. Most of the adsorbents are used without any treatment such as orange peels (Sivaraj *et al.*, 2001), agrowastes (Okeola & Odebunmi, 2010), banana peel (Ali and Saeed, 2015), *Acacia nilotica* leaf (Santhi *et al.*, 2014), pine needles (Malik *et al.*, 2015), cashew nut shell (Subramaniam &

Ponnusamy, 2015). The plant based adsorbents are lignocellulosic materials and applied in the elimination of dye, heavy metals, phenol and other organic pollutants. Generally, these materials are considered as low cost due to cheap in nature, wider and locally availability and most abundant in nature.

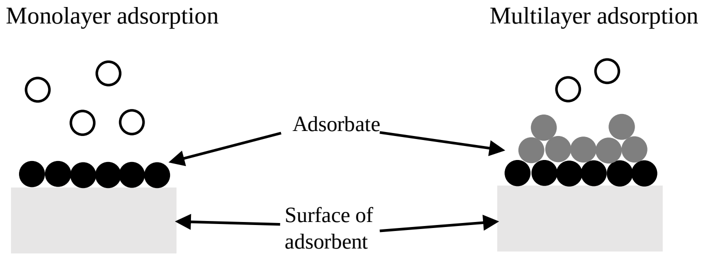
The quality of adsorbate that can be taken up by an absorbent is a function of both the characteristics and concentration of adsorbate and the temperature. The characteristics of the adsorbate are considered important including molecular structure, solubility, molecular weight, polarity and hydrocarbon saturation (Li *et al*., 2002). The molecular structure determines the accessibility of the adsorbate to the pores of the adsorbents, the solubility determines the degree of hydrophobic interactions between the adsorbate and the adsorbent surface, and the polarity and hydrocarbon saturation determine the ability to withdraw or release electrons, which therefore affects the non-electrostatic interactions between the adsorbate and the adsorbent surface (Moreno-Castilla, 2004).

The function of the concentration at a fixed temperature is usually controlling the amount of the substance adsorbed and the resulting function is so-called an adsorption isotherm. This isotherm is defined by explicated the quantity of adsorbate adsorbed per unit mass of adsorbent, q. Meanwhile, function of C is the concentration of adsorbate remaining in solution. The equation 2.1 was used to determine the adsorbent phase concentration after equilibrium which are the amount of adsorbate adsorbed at equilibrium:

$$q_e = \frac{(C_o\text{-}C_e)V}{m} \tag{2.1}$$

where q_e is the amount of adsorbate adsorbed after equilibrium (mg/g), C_o is the initial adsorbate concentration (mg/L), C_e is the final equilibrium adsorbate concentration after adsorption (mg/L), V is volume of solution in the reactor (L) and m is mass of adsorbent (g) (Stumm & Morgan, 1995).

The adsorption equilibrium isotherm is an important parameter to consider in the design and operation an adsorption system. The nature of an isotherm gives the evidence about the attraction of the adsorbate toward the adsorbent and provides an idea of the adsorption capacity (Dawood & Sen, 2012; Pathak & Mandavgane, 2015). There are several types of adsorption models have been commonly used in the adsorption studied to explain the adsorption phenomena, for example, Langmuir and Freundlich isotherm models (Crittenden & Thomas, 1998; Edzwald, 2011). Langmuir isotherm model proposed that the adsorption process occurs on the monolayer surface of the adsorbent. The maximum adsorption capacity per unit adsorbent mass is determined along with the Langmuir constant showing the solute affinity to the adsorbent. Meanwhile, the Freundlich type adsorption is assumed that the amount of adsorbate adsorbed per unit adsorbent mass rises progressively and to be a multilayer process.



(a) (b)

Figure 2.4: The assumption of (a) Langmuir and (b) Freundlich adsorption models

The Langmuir isotherm can be expressed by using the following Equation 2.2:

$$q_e = \left(\frac{K_L C_e}{1+ K_L C_e}\right) q_{max} \tag{2.2}$$

where K_L is the constant of the Langmuir isotherm (L/mg) and q_{max} relates to the maximum amount of solute adsorbed or the adsorption capacity (mg/g). The equation 2.2 may be reformulated in the form of linear equation 2.3:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{K_L q_{max} C_e}\right) \tag{2.3}$$

The Freundlich isotherm can be firstly developed as an empirical model, may be expressed in equation 2.4:

$$q_e = K_F C_e^{1/n} \tag{2.4}$$

where K_F is the Freundlich isotherm constant (L/mg) and $1/n$ is the Freundlich exponent.

The linear form of Freundlich isotherm can be formulated as follows:

$$loq\ q_e = log\, K_f + \frac{1}{n}\, log\, C \tag{2.5}$$

In order to represent the ability of adsorbents to adsorb the pollutant from a waste, it is important to determine the adsorption isotherm. The description of the functional requirement of capacity on the concentration of pollutant is offered by the adsorption isotherm. If the isotherm is steeper, the adsorbent become more operative because the isotherm have a sharp rise to a given ultimate capacity by way of concentration increases, the effective capacity at the concentration level desired for the treated water will be higher (Dabrowski, 2001).

In spite of adsorption equilibrium studies, the identification the mechanism type of adsorption in a given system is also important. Adsorption kinetic models have been used to discover the possible rate-controlling steps included in the adsorption process, for example chemical reaction, mass transport and diffusion control (Ahmad & Kumar, 2010; Santhi *et al.*, 2014). In order to understand the adsorption kinetics and rate limiting step, there are a few adsorption kinetic models that have been recognized. Among those kinetic models, pseudo-first-order and pseudo-second-order kinetic rate model are the most well-known model used in the adsorption kinetic studies.

The pseudo-first-order kinetic model assumed that the amount of change of solute adsorb is directly proportional to the amount of solute uptake and also difference in saturation concentration over time. Meanwhile, the pseudo-second-order kinetic model is according to the hypothesis that chemisorption involving valency forces. The process happens by exchanging or sharing of electron between adsorbent and adsorbate is the rate-limiting step. Besides that, this model is a model to study the behaviour of the whole adsorption process (Zhang *et al.*, 2014; Mohan *et al.*, 2006).

The linear equations of pseudo-first-order model is expressed as:

$$log\ (q_e - q_t) = log\, q_e - \frac{k_1}{2.303} t \tag{2.6}$$

Meanwhile, the pseudo-second-order kinetics model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2.7}$$

where q_t is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g) at time t, k_1 is the pseudo-first-order rate constant (min^{-1}), t is the shaking time (min) and k_2 is the pseudo-second-order rate constant (g/mg.min).

2.3 Modification of Adsorbents

The modification method of adsorbents has effect on the factors such as surface functional group, surface morphology, specific surface area, pore-size distributions, pore volume and surface charging which are influences the efficacy of the adsorption capacity of the adsorbents. As the specific surface area increases, the adsorption capacity also increases due to the availability of a number of adsorption sites. At the same time, the composition of the adsorbents are related to the pore size and micropores distribution of the adsorbents (Ruthven, 1984).

The surface of adsorbent can be modified to improve required physico-chemical properties of adsorbent by suitable choice of activation procedures. There are three methods of modification of adsorbent which are chemical, physical and biological modifications. Modification by chemical means consist of acidic treatment, basic treatment and impregnation of external materials. Besides, heat treatment are one of the modification methods of physical characteristics. Meanwhile, one of the example of modification of biological characteristics of adsorbents is bioadsorption treatment (Gautam *et al.*, 2014).

2.3.1 Acidic Treatment

Modification of adsorbent by acidic treatment is commonly used to oxidize the surface of adsorbent. The treatment can increase the acidic functional groups on the adsorbent surfaces and eliminates the mineral elements as well as develops the hydrophilic surface nature of adsorbents (Shen *et al.*, 2008). The most widely used chemical in acidic treatment of adsorbents are sulfuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3) and phosphoric acid (H_3PO_4). According to Huang (1996), modification of adsorbent by acidic treatment can clean-up the surface impurities as well as opening the available sites on the surface hence increase the adsorbents surface area in order to enhance the adsorption.

The adsorption of anionic dye Congo red was examined with hydrochloric acid (HCl) modified pine cone powder adsorbent (Dawood & Sen, 2012). In order to prepare acid modified pine cone powder adsorbent, 10 g of raw pine cone powder was soaked in 100 ml of M HCl solution. Findings revealed that the specific surface area was increased and the mean particle size was reduced after acidic treatment of pine cone. The specific surface area of acid-treated pine cone was 0.122 m^2/g and the mean particle size was 49.03 µm. Meanwhile, the adsorption capacity of acidic modified pine cone was increased to 40.19 mg/g, which is 7.54 mg/g higher than the raw pine cone adsorbents.

Ahmad and Kumar (2010) reported the effectiveness of ginger waste treated with sulfuric acid (H_2SO_4) and zinc chloride ($ZnCl_2$) towards the malachite green dye removal from aqueous solution. The ginger waste was soaked for 24 hours in a solution prepares from H_2SO_4 and $ZnCl_2$ in the ratio of 1:1. The results showed that the adsorption capacity was increased from 4 to 15.5 mg/g with the increase in dye concentration from 5 to 20 mg/L. Meanwhile, the results showed that both Langmuir and Freundlich models can be used to fit the experimental data and to estimate the models parameters. From the study, the researchers have concluded that the acidic treatment of ginger waste can enhance the adsorption capacity of the malachite green dye.

The effect of acidic treatment on activated carbons for three different dye (methylene blue, rhodamin B and crystal violet) adsorption was investigated (Wang & Zhu, 2007). It was revealed that more active acidic surface groups on the HNO_3 treated adsorbent for example, carboxyl and lactone. The acidic group can cause a decrease in the adsorption of basic dyes. However, HCl treatment reduced active acidic groups and hence enhanced the adsorption of larger dye molecules on activated carbon. The results presented the differences of the adsorption behaviour due to the different functional groups of dyes.

2.3.2 Alkaline Treatment

In order to produce positive surface charges which can help to adsorb high amount of negatively charge species, alkaline treatment on adsorbents is commonly used (Bhatnagar *et al.*, 2013). Furthermore, alkaline treatment of adsorbent also enhance the uptake of organics and metals ion adsorption in many cases. Sodium hydroxide (NaOH), ammonia (NH_3) and potassium hydroxide (KOH) are the most commonly utilized alkali for the alkaline treatment of adsorbent and activated carbon (Argun *et al.*, 2009, Afkhami *et al.*, 2007, Mangun *et al.*, 2001).

The adsorption of methylene blue and methyl green was explored with NaOH treated timber sawdust (Djilali *et al.*, 2012). The study suggested that the timber sawdust with alkaline treatment can enhance the amount of basic dyes adsorbed. Furthermore, the treatment of timber sawdust with aqueous NaOH allows the extraction of hemicellulose and most part of lignin as well as enhance the alteration of the polyol structure into a negatively charged cellulose-based materials. The material bears a huge number of negatively charged sites in the surface of adsorbent favouring the adsorption of cationic dyes through electrostatic attraction.

Researchers suggested that the activation of charcoal by alkaline treatment can produces pores and voids. The treatment also can create greater surface area in the carbon materials, thus can enhance the adsorption capacity. A study of the adsorption of the KOH activated biomass from bamboo had been investigated (Lalhruaitluang *et al.*, 2011). The raw charcoal was treated with various concentration of KOH from 10 to 18 % of concentration. The finding of study revealed that the highest adsorption of Ni (II) and Zn (II) were achieved at the KOH concentration of 50% and 60% treatment.

The adsorption study of five different dyes from an aqueous solution was observed on three different low cost pre-treated agricultural residues i.e., wheat straw, corncob and barley husk. The pre-treatments with steam, NaOH and NH_4OH were carried out on the agricultural residues in order to enhance the surface area of adsorbents and to determine their effects on the rate and effective adsorption of dyes. The results revealed that higher percentage of dye removal were accomplished by NaOH and NH_4OH treated wheat straw and barley hulk (Robinson, 2002).

Recently, the combination of acid and alkaline treatment in the modification of adsorbents and activated carbon was studied among researchers. Fathy *et al.*, (2013) were studied the effectiveness of alkali-acid modification in enhancement the adsorption capacity of rice straw for removing basic dye, methylene blue. From the results, the chemical treatment had a remarkable effect on the physicochemical properties of the produced rice straw adsorbents. Upon the treatment, a reactive anhydride was yield which can react with the starch or cellulosic hydroxyl groups resulting in an ester-linkage and introduce free carboxyl groups to adsorbent surface, thereby enhancing the binding of cationic dye.

2.3.3 Microwave Treatment

Microwave treatment has been widely used as an alternative heating method and some studies have proved that microwave treatment can be successfully employed in the production of adsorbent (Hirata *et al.*, 2002). Previously microwave is only extensively used as household appliances in most homes, conveniences store and restaurants due to the reduction time, energy saving and low operating cost during cooking. Microwave oven uses radio waves to heat food and it works by passing non-ionizing microwave radiation through the food. The commonly used radio wave frequency in microwave oven is about 2.5 gigahertz (Lee, 2000).

The properties of radio waves in this frequency can be adsorbed by water, fats and sugar. After that, the waves are directly converted into atomic motion and then the motion are converted into heat. The process is called dielectric heating. Fats and sugar adsorb microwave because of the dipole moments of their hydroxyl group or ester groups. The waves often achieve higher temperatures inside microwave ovens since the specific heat of fats and oils are lower as well as their vaporization temperature is higher (Caplin and Martin, 2012). The microwave heating happens over the conversion of electromagnetic energy into heat inside the irradiated materials. Compared to conventional heating, they offer several benefits, for example, rapid heating, selective materials heating, volumetric heating, non-contact heating, energy transfer instead of heat transfer, quick start-up and stopping, heating from the interior of the materials body and higher level of safety and automation (Haque, 1999).

In general, carbon can be basically created or changed by microwave heating since they are great microwave absorbers as compared to other solid materials (Menendez *et al.*, 2010). In past few years, microwave heating has been effectively used for the preparation of activated carbon (Emine *et al.*, 2008; Foo and Hameed, 2011). As compared to conventional heating, the main advantage of using microwave in the case of granular activated carbons are in term of time and energy saving, as the chemical change observes on the carbon surface did not differ very much regardless of the method used, provided that similar temperatures were used (Menendez *et al.*, 1999). Microwave supplies energy to the carbon particles, then it changed into heat within the particles themselves by ionic conduction and dipole rotation. The microwave heating also can modify the surface of activated carbon and carbon fibers (Carrott *et al.*, 2001).

In recent research by Zhang *et al.* (2013), they suggested that microwave treatment gave effect on the texture of pore of the activated carbon. The activated carbon presents a high temperature rise and the carbon skeleton is contracted during the microwave heating, thus changes the pore structure of the activated carbon. The contraction and shrinkage of carbon skeleton has same effects on the pores. The microwave heating also gave effect on the average width of the pores because the pores with different width are shrank during microwave heating. Meanwhile, microwave modified activated carbon from bamboo-based has been studied (Liu *et al.*, 2010). After modification, the miropores were increased in the beginning and then stretched into greater ones, causing the average pore size and pore volume to increase. A decrease in the surface acidic groups and increase in the surface basicity were also observed. The surface basicity was enhanced to a rise in the point of zero charge, pH_{pzc}. The pH at which the surface charge is zero is called the point of zero charge (pzc) and is typically used to quantify or define the electrokinetic properties of a surface (Liu *et al*., 2012).

Previous study by Pathak and Mandavgane (2015) showed that the surface of adsorbent from banana peel increased from 0.65 m^2/g to 22.37 m^2/g which is 34.41 times more. The surface of microwave activated banana peel is also rough and porous due to microwave treatment. Raw banana peels were activated by keeping inside a modified microwave oven (Panasonic NN78 4MF) and heated at full power (1200 W) for 10 min. Another study was made by Njoku *et al.*, (2013) on activated carbon prepared from pumpkin seed hull microwave induced KOH activation. The char pumpkin seeds hull was prepared in a glass reactor inside a modified microwave oven under nitrogen flow of 300 cm^3/min and 600 W input power with irradiation time of 12 min. The result of Langmuir surface area, BET surface area and total pore volume was presented to be 1087.00 m^2/g, 737.90m^2/g and 0.370 cm^3/g, respectively. The pore diameter of the activated carbon also indicated that almost all of the pores fall into the characteristic of mesopores.

2.4 Characterization of Adsorbent

2.4.1 Morphological Properties

In the study of textural morphology of adsorbents, many researches have widely used scanning electron microscope (SEM). SEM is a microscope that uses electron to form an image. By using SEM, researchers can observe much bigger range of specimens because it has a huge depth of field which permits more of a specimen to be focus at one time. The higher resolution of SEM allows closely spaced specimens to be magnified at much greater levels. Besides that, the researchers has much more control in the degree of magnification because of the electromagnets uses rather than lenses in the SEM (Schweitzer, 2010). According to Australian Microscopy and Microanalysis Research Facility (AMMRF), SEM can magnify an object from 10 up to 300,000 times. The formation of image in the SEM is depended on the acquisition of signals produced from the electron beam and specimen interactions

According to a recent study, SEM was used to determine the textural morphologies of the pamelo skin activated carbon (PSAC) and the char. The SEM micrographs showed the surface of PSAC was well developed and definite pores over the surface, meanwhile, the surface of char was dense (Foo and Hameed, 2011). In another study by Liu *et al.* (2012), the SEM images displayed the structures and morphological characteristics of the feather and feather activated carbons (FACs). The pores of FACs are mostly micropores with a less percentage of mesopores, while the feathers showed an image of a smooth surface and limited number of cavities.

2.4.2 Surface Functional Group of Adsorbent

The surface functional groups of adsorbent was widely discovered by using Fourier Transform Infrared (FTIR) spectroscopy. FTIR was used to determine an emission, infrared spectrum of adsorption, photoconductivity or scattering of a solid, liquid or gas (Griffiths and Haseth, 2007). According to Thermo Nicolet Corporation (2001), the infrared radiation is passed over the sample as well as some of the radiation is adsorbed by the sample and transmitted through the sample. A molecular fingerprint of the samples was created from the spectrum which is represent the molecular adsorption and transmission. Therefore, FTIR spectroscopy becomes more useful for several types of analysis.

In previous study by Singha *et al.* (2011) the utilization of natural adsorbents for Cr (VI) ions elimination from aqueous solutions was investigated. In this study, the changes in vibration frequency of the functional group of the adsorbent because of Cr (VI) adsorption was determined by using FTIR. Each fresh and Cr (VI) loaded adsorbents were mixed individually with potassium bromide (KBr) of spectroscopic grade. The mixture was made in the form of pellets at a pressure of about 1 MPa. The pellets were about 1 mm thickness and 10 mm in diameter. After that, the adsorbents were scanned by using FTIR spectroscopy in the spectral range of 4000 - 400 cm^{-1}. From this study, the FTIR spectra of the adsorbents showed a few number of adsorption peaks presenting the complex nature of the adsorbents. Therefore, the determination of functional group changes from the FTIR spectra are important factors in order to recognize the mechanism of the metal or adsorbate binding process on the adsorbent.

Previous study by Yang and Cui (2013), Fourier transform infrared spectroscopy (FTIR) analysis revealed that carboxyl and hydroxyl functional groups were mainly responsible for the adsorption of Pb (II) onto alkali treated tea residues. The shifts of bands at 3412, 2919, 2850, 1634, 1373 and 1059 cm^{-1} to 3399, 2920, 2851, 1636, 1383 and 1058 cm^{-1} respectively might be attributed to ion exchange associated with carboxylate and hydyroxylate anions, suggesting that acidic groups, carboxyl and hydroxyl, were predominant contributors in metal ion uptake. Another study by Gupta *et al.*, (2011) on the application of potato (*Solanum tuberosum*) plant wastes for the removal of methylene blue and malachite green dye from aqueous solution showed that the broad FTIR absorption peaks around 3400 cm^{-1} was due to vibration of the hydroxyl group linked in cellulose and lignin and adsorbed water. Besides that, the C–O stretching band at 1246 cm^{-1} also confirms the lignin structure of the adsorbents and corresponding bending peak present around 600 cm^{-1}. The peak around 1050 cm^{-1} was due to C–O–C stretching of cellulose present in potato plant wastes which contributed to the binding of the dyes.

2.4.3 Surface Area and Porosity

The determination of surface area and porosity of adsorbent are an important method for the production of effective adsorbent. The Brunauer-Emmett-Teller (BET) method is the most commonly used method for the determination of the surface area of solid materials. According to Hwang and Barron (2011), the theory of BET was introduced by Stephen Brunauer, P. H. Emmett and Edward Teller in 1938. It was developed during their study on ammonia catalyst. The aim of the study was to state the specific surface of finely divided and porous solids.

In a previous study on pamelo skin activated carbon, the porosity of carbonaceous adsorbent was determined by using nitrogen adsorption technique. It was found that the isotherm displayed by an arrangement of microporous and mesoporous structures. The isotherms represented micropores slope of the plateau at high relative pressure which was because of the multilayer adsorption on the external surface. The specific surface area was calculated by the BET equation:

$$\mathrm{r} = \frac{4\mathrm{V_T}}{\mathrm{S_{BET}}} \tag{2.8}$$

where S_{BET} is the specific surface area, V_T is the total pore volume that evacuated by altering the adsorption volume on nitrogen at relative pressure 0.95 to equivalent liquid volume of adsorbate and r is the average pore size.

A study of the adsorbent from low-cost chlorella-based biomass for the elimination of malachite green dye from aqueous solution was investigated (Tsai and Chen, 2010). In this study, the biomass physical characteristic and carbon adsorbents were determined by measuring its nitrogen adsorption-desorption isotherms at 77K in a surface area and porosity analyser (Model No.: ASAP 2020; Micromeritics Co., USA). The surface area and porosity characteristics were also investigated by some researchers onto other waste materials such as microalgae waste (Ferrera-Lorenzo *et al.*, 2014), grape stalk (Ozdemir *et al.*, 2014), wool waste (Gao *et al.*, 2013), and sawmill waste (Sinha *et al.*, 2015) have been investigated as adsorbents.

2.4.4 Surface Charging of Adsorbent

According to Medical Textile Laboratories of North Carolina State University (2016), the electrokinetic analyser is used to help material scientist to change surface characteristics and develop new specialized material characteristics. The analyser is used for materials such as polymers, ceramics, textiles, glass or surfactants. By using the analyser, the electrokinetic effects at the solid or liquid interface for solid can be investigated at almost any size and shape.

Particles Science Incorporation (2012) stated that the zeta potential is provided by electrokinetic analyser and allow researchers to study liquid-on-solid adsorption processes by measuring the streaming potential or streaming current of macroscopic solids. Zeta potential is an interfacial property that important for understanding the behaviour of solid materials in many technical processes. It offers understanding into the charge and adsorption properties of solid surfaces.

2.5 Dye Solution

Dyes are organic compounds that can be utilized to give bright and permanent colours to fabric. There are about 100,000 commercially dyes with over 735 tonnes of dyestuff manufactured annually (Yagub *et al*., 2014). Dyes are tough to disappear on the contact of light, water and many other chemicals because of their chemical structure. The attraction of dye for fabric influences by the interaction of chemical structure of dye and fabric molecules. Therefore, the chemical bonding of the dyes is important to give a function to the dyes on the fabric (Robinson *et al*., 2001). Dye and dyestuffs are used in a widespread range of industries but they are become important material to textile manufacturing. Wastewater from the textile industries are complex mixture of many polluting substances. Large amount of the dyestuff misplaced to the wastewater and directly into environment when inefficiencies in dyeing during the textile processing (Selvakumar *et al*., 2013).

Homemade textile industry, batik industry in Malaysia is well known mainly in the East Coast of Peninsular Malaysia and Sarawak. High skills with better equipment and tools are required to produce high quality of batiks. Nowadays, the batik industry has become much commercialized. The industry has contributed positively to the economic growth for Malaysia (Kheng, 1998). During the last stage of batik processing, which is boiling process, the boiled water that containing the dye are normally discharge as wastewater from batik industry. Ahmad *et al*. (2007) have stated in their study that without further treatment of the wastewater from batik industry, it may contribute to water pollution thus give negative effects to the environment.

Wastewater from textile industry is basically rich in colours that comprising residues of reactive dyes and chemicals, for example, aerosol, complex components, high BOD and COD concentration. They also contain a great total of hard-degradation properties. The dyestuffs and other organic compounds also contain toxic, alkaline and acidic pollutants which are widely accepted on the general public. Recently, most of the dyes are heterocyclic and aromatic compounds with colour display and polar group. The dyeing wastewater become more difficult to degrade because the structure of the dyes are complicated and stable, hence, high amount of dyeing wastewater released to river or stream (Savin & Butnaru, 2008).

2.5.1 Malachite Green

Malachite green (MG) is a dye from triphenylmethane family which is water-soluble dye that has commonly used in dyeing processes for wool, silk, leather and cotton. It also has been used as antifungal therapeutic agent in commercial dish hatchery, aquaculture and animal husbandry. MG dye also has been used as antiseptic and fungicidal for human (Sawa *et al.*, 2001). MG dissociates into anion and cation colours, where the electrostatic attraction develops among the coloured cation and acidic groups of acrylic fibres lead to procedure salt and change the colour fade upon the fabrics (Syed, 2011).

The chemical structure of MG dye as shown in Figure 2.5. MG dye has solubility of 60mg/ml in water at 20°C with chemical formula of $C_{23}H_{25}ClN_2$ and molar mass of 364.911 g/mol contains of toxic characteristics which are recognized as carcinogenesis, mutagenesis, teratogenesis and respiratory toxicity (Srivastara *et al.*, 2004). When the intense colour of dyes interferes with sunlight and entering the water bodies, the photosynthesis rates will be decreased drastically (Beak *et al*., 2009). Therefore, it is important to remove MG from wastewater before discharging to the environment.

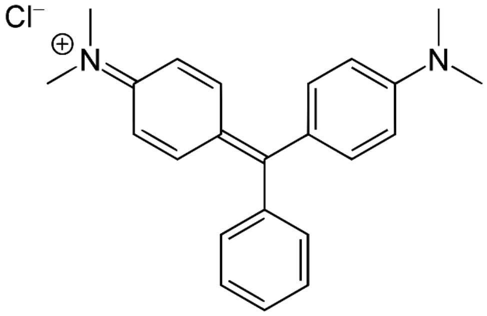


Figure 2.5: Chemical structure of malachite green

Recently, elimination of MG from the dyeing-based wastewater effluents by employing numerous physical techniques such as adsorption, chemical methods and biological methods has been suggested. Adsorption method by using low cost adsorbents for example from poultry, agricultural waste and industrial waste are the most simple, economical and widely employed method to remove MG from the aqueous solution (Ahmad & Kumar, 2010; Gupta *et al*., 2011; Chaturvedi *et al*., 2013; Magriotis *et al*., 2014).

A study was conducted using a multifunctional strain of *Pseudomonas mendocina* PM2 to degrade a high amount of MG and metabolised chicken feathers as carbon and nitrogen sources. MG is known as a recalcitrant dye which can be adsorbed on surface of chicken feathers. Results demonstrated that decolourization and degradation of high amounts of MG which up to 1800 mg/L. It proved that strain PM2 decolourize MG and also simultaneously metabolize malachite green adsorbed chicken feathers (Chaturvedi *et al*., 2013). Kushwaha *et al*. (2014) examined the elemination of cationic dye methylene blue and MG from aqueous solution using waste material from *Daucus carota* plant (carrot plant). Methylene blue and MG was used to study due to their wide applications in colouring paper, dyeing cottons, wools, leather and silk. The variables, for instance, pH and concentration of dye were examined. From the results, it showed *Daucus carota* plant wastes were successfully used for the MG dye from the aqueous solution.

2.5.2 Neutral Red

Neutral red (NR) or toluylene red is used for discolouration in histology. The NR dye is a eurhodin dye and used as counter strain in mixture with other dyes and for many discolouration methods. NR can be used to colour embryonal tissues as well as supravital discolouration of blood when it comes together with Janus Green B. It is also utilized for discolouration Nissl granules in neurons and Golgi apparatus in cells. In microbiology, NR is utilized in the MacConkey agar to separate bacteria for lactose fermentation (Repetto *et al.*, 2008).

The IUPAC name of NR dye is 3-amino-7-dimethylamino-2-methylphenazine hydrochloride having the chemical formula for this dye is $C_{15}H_{17}ClN$ and chemical structure as shown in Figure 2.6. NR has a molar mass of 288.78 g/mol and melting point of 290°C. The solubility of NR in water is 10mg/ml. Neutral red can act as pH indicator, whereby when the pH in between 6.8 to 8.0, the colour are turning to yellow.

Like other dyes, NR are also toxic and hazardous to human (Pourreza & Narunpghdi, 2011). The toxic way of the dye can be simplified by giving out hazardous products, for example carbon dioxide (CO_2), carbon monoxide (CO), hydrogen chlorides and nitrogen oxides. Therefore, they must be removed before entering the environment.

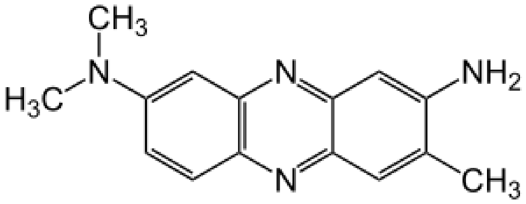


Figure 2.6: Molecular structure of neutral red

The adsorption of cationic NR dyes onto peanut husk in aqueous solutions was explored (Han *et al.*, 2008). The results showed the optimal pH for the favourable adsorption of dyes was within the range of 5 to 7. The removal of dye was enhanced and when the adsorbent dosage was increased the removal of dye achieved maximum values. In this study, the researchers concluded that NR dyes can be eliminated by using peanut husk. Another researchers have been studied on the removal and separation of NR onto acid-treated pine sawdust (Pourreza & Naghdi, 2011). The factors on the pH solution, dye concentration, particle size of the adsorbent and adsorbent dosage was investigated. The highest removal of NR were obtained at pH 5.25 and using 0.3 g of adsorbent. From the results, the removal and separation method was successfully applied for NR-spiked tap and river water samples.

CHAPTER 3

RESEARCH METHODOLOGY

This chapter explains about the material, equipment and apparatus used in this research. It also describes the methodology applied for the characterization and application of the adsorbent in the adsorption of dye. Besides, this chapter expresses the formulas and equations for the finding of this research. It also explains the modelling used for the experimental data in this research.

3.1 Materials

C. equisetifolia seeds used in this study were obtained from Pantai Teluk Ketapang, Kuala Terengganu in Terengganu. The seeds were collected around 3 metres radius of a selected *C. equisetifolia* tree in order to obtain the same characteristics of seeds and it was collected between October and November 2014.

3.2 Preparation of adsorbent

There were three types of adsorbents used in this study i.e., untreated (as control), acid-alkali treated and microwave-acid-alkali treated adsorbents. *C. equisetifolia seeds* were washed repeatedly with distilled water to eliminate adhering dirt and dried in an oven at 70°C for 12 hours. The seeds were weighted before and after dried in order to make sure the moisture content and water were fully dried from adsorbents. The seeds were ground and sieved into small particles of about 1mm to 3 mm. The ground seeds were readily to be used as untreated adsorbent.

In the preparation of acid-alkali treated adsorbent from *C. equisetifolia* seeds, the ground seeds were treated using 1 M of *p*-toluene sulfonic acid monohydrate solution in the 1:2 of adsorbent and acid solution ratio for 24 hours. Then, the acid-treated seeds were dried for 12 hours in the oven at 70°C. The acid-treated seeds were then soaked in 0.1 M of sodium hydroxide (NaOH) solution in the ration of 1:2 for 24 hours. The treated seeds were dried for 12 hours in an oven at 70°C. The ratio 1:2 was used in to ensure the adsorbents had fully immersed in the acid and alkali solution.

Meanwhile, for the preparation of microwave-acid-alkali treated adsorbent from *C. equesetifolia* seeds, the seeds were first treated in microwave oven with frequency of 2.34 GHz, 800 W and 8 min of irradiation time was selected as the heating period based on preliminary runs and in order to prevent the seeds to be burnt. After that, the seeds were treated by using *p*-toluene sulfonic acid monohydrate and NaOH solution. Acid-alkali treatment of adsorbents was applied after microwave heating in order to remove the amorphous carbon and silica from adsorbent resulting in porous structure and a corresponding increase in the surface area (Gautam *et al*., 2014).

In this research, microwave treatment was used to activate the surface of adsorbents from *C. equistifolia* seeds. For the acid treatment of adsorbent, *p*-toluene sulfonic acid monohydrate was used due to its characteristic as green chemical. The acid treatment onto *C. equisetifolia* seeds would not remove the important functional group, yet it could introduce new carboxyl group to adsorbent surface (Fathy *et al*., 2013). Meanwhile, NaOH was used in this experiment because alkali solution like acid modification can increases the efficacy of adsorption because of the increase of negatively charged hydroxyl anions (Argun *et al*., 2009). The combination of both acid and alkali in the preparation of adsorbent was also studied by Fathy *et al*., (2013) which can enhance the effectiveness of the adsorbents hence improve the adsorption capacity of the dyes.

3.3 Preparation of adsorbates/dyes

In this study, malachite green (MG) and neutral red (NR) dyes, in powder-form were used as synthetic dye wastewater for the adsorption onto *C. equisetifolia* seeds. These dyes were supplied by Bendosen Laboratory Chemicals. MG is a cationic dye with molecular weight of 364.911 g/mol, chemical formula of $C_{23}H_{25}ClN_2$, and maximum wavelength (λ_{max}) of 618 nm. Meanwhile, NR is also a cationic dye and has molecular weight of 288.78 g/mol, chemical formula of $C_{15}H_{17}ClN$ and λ_{max} of 540 nm. Both dyes were obtained from Bendosen Laboratory Chemicals. Before absorbance of the dye was determined, the λ_{max} of the dye was set in the spectrophotometer and the λ_{max} is known as the absorption spectrum of the solution.

For the preparation of standard curve, a series of 10 mg/L to 50 mg/L of the concentration of dye were diluted. For the preparation of dye solution in order to conduct batch adsorption experiment, an amount of required mass of dyes were diluted in 1000 ml of distilled water. In the batch adsorption experiment for the effect of dye concentration, the concentration of dye used were in between 200 mg/L to 400 mg/L. Meanwhile, a fixed concentration of dye (200 mg/L) were used in the batch adsorption experiment for the effect of adsorbent dosage.

3.4 Characterization method

3.4.1 Surface morphology of adsorbent

The Scanning Electron Microscopy (SEM-JEOL-6360 LA) as shown in Figure 3.1 was used to study the surface morphology of adsorbent from *C. equisetifolia* seeds. The microscopy was located at Scanning Electron Microscopy Unit Laboratory of the Institute of Oceanography and Environmental (INOS), UMT. The sample from *C. equsetifolia* seeds was mounted on metal stub and coated with gold before it was examined under SEM. The SEM images of adsorbent from *C. equisetifolia* seeds were viewed under magnification of 200x, 500x and 1000x.

Figure 3.1: Scanning electron microscopy (SEM)

3.4.2 Chemical characterization of adsorbent

The SHIMADZU IRTracer-100 Fourier Transform Infrared Spectroscopy (FTIR) as shown in Figure 3.2 was used to determine the chemical functional group of adsorbent from *C. equisetifolia* seeds. The spectroscopy was located at the Physic and Instrumentation Laboratory at UMT. The sample was directly put on the detector of the spectroscopy, since the preparation of sample for this type of spectroscopy does not required KBr mixture. The infrared spectra for the adsorbents were recorded on FTIR Spectroscopy in the range of 4000 to 400 cm^{-1}. In order to identify the differences between adsorbents, the FTIR spectra of the adsorbent from raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds were analysed.

Figure 3.2: Fourier Transform Infrared Spectroscopy (FTIR)

The chemical compositions analyse of *C. equisetifolia* seeds were carried out at Forest Research Institute Malaysia (FRIM). The experiment on Ethanol-toluene solubility, Hot water solubility, Alkali solubility, alpha-cellulose content, lignin content and Ash content of *C. equisetifolia* seeds were carried out according to TAPPI Standard T264 cm-97 (TAPPI, 1007), T207 cm-9 (TAPPI, 1991), T212 om-02, T203 om-93, T222 om-02 and T211 om-02 (TAPPI, 2002), respectively. Otherwise, the method developed by Wise had been used in the determination on holocellulose content (Wise *et al*., 1946). The experiments performed to identify the chemical compositions are shown in Appendix A.

3.4.3 Physical characterization of adsorbent

The physical characteristics of adsorbents from *C. equisetifolia* seeds were determined by using surface area and porosity (BET) analyser (ASAP 2020 MICROMERITICS). The physical properties were included the BET surface area, pore volume and pore sizes of the adsorbents.

3.4.4 Surface charging of adsorbent

SurPASS Electrokinetic Analyser was used in order to investigate the surface charging of the adsorbents from *C. equisetifolia* seeds. The analyser as shown in Figure 3.3 was provided at Water and Wastewater Engineering Laboratory at UMT, and the analyser provides the zeta potential by measuring the streaming potential or streaming current of macroscopic solids and allows to study the liquid on solid adsorption processes.

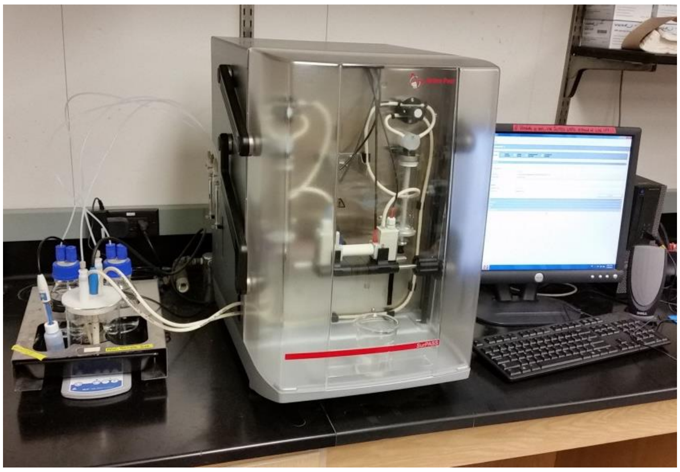


Figure 3.3: Electrokinetic analyzer

3.5 Batch adsorption experiment

The batch experiment was carried out by using three types of adsorbents i.e., untreated, acid-alkali treated and microwave-acid-alkali treated *C. equisetifolia* seeds. A series of experiments were conducted to determine the effect of contact time, initial dye concentration and adsorbent dosage on the percentage of dye removal and the amount of dye adsorbed. In order to ensure the reproducibility of the obtained results, all the adsorption experiments were performed in triplicate and the average values were used in data analysis. The percentage of dye removal were calculated as follows:

$$\%\ Dye\ removal = \frac{C_0 - C_e}{C_0} \times 100 \qquad (3.1)$$

where C_0 is the initial dye concentration (mg/L) and C_e is the equilibrium dye concentration (mg/L). Meanwhile, the amount of dye adsorbed by the adsorbent were determined as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (3.2)$$

where q_e is the amount of dye adsorbed or adsorption capacity at equilibrium (mg/g), V is volume of dye solution (L) and m is mass of adsorbent (g)

3.5.1 Effects of contact time

The effects of contact time on the adsorption of MG and NR dyes were investigated at 200 mg/L of initial dye concentration and 0.4 g of adsorbent dosage. 250 mL of conical flask was filled with 100 mL of dye solution and 0.4 g of adsorbent dosage, then the mixture was shaken in water bath at 125 rpm and under room temperature. The uptake of dye was analysed at 0 to 240 minutes. The absorbance of solution was measured by using Spectrophotometer and from the absorbance, the final concentration of the dye was calculated by referring the standard curve of the dyes (as shown in Appendix B), meanwhile the percentage of dye removal was calculated by using the Equation 3.1.

3.5.2 Effects of initial dye concentration

In this experiment, 200, 300 and 400 mg/L of initial dye concentration were used and 0.4 g of adsorbent was used as a fixed adsorbent dosage. 0.4 g of adsorbent dosage was selected because in order to make sure the percentage of dye removal between the initial dye concentrations were found in the appropriate range. 100 mL of dye solution was added into 250 mL conical flask containing adsorbent. The mixture was shaken under room temperature using water bath shaker at 125 rpm until reaching equilibrium. At known time interval, 5 mL samples of solution were taken from conical flask and the absorbance of the solution was measured by using Spectrophotometer. From the absorbance values, the final concentration of the dye and the amount of dye adsorbed were calculated by referring to the standard curve of the dyes (as provided in Appendix B). Meanwhile the percentage of dye removal and the amount of dye adsorbed were calculated by using the Equation 3.1 and 3.2, respectively.

3.5.3 Effect of adsorbent dosage

For this experiment, 0.2 g – 1.0 g of adsorbent was used in order to study the effect of adsorbent dosage and 200 mg/L of dye solution was used as a fixed dye concentration. 100 mL of dye solution were kept in the 250 mL of conical flask that contained adsorbent. The flask was kept in the water bath shaker at room temperature mechanically shaken at 125 rpm until reaching equilibrium. The absorbance of solution was measured using Spectrophotometer by withdrawing 5 mL of dye solution from conical flask at known time interval. From the absorbance, the final concentration of the dye was calculated by referring the standard curve of the dyes (as shown in Appendix B), and the percentage of dye removal and the amount of dye adsorbed was calculated by using the formula as shown in Equation 3.1 and 3.2, respectively.

3.6 Adsorption equilibrium studies

Equilibrium studies were conducted by mixing 0.4 g of adsorbent with different initial dye concentration of 200, 300 and 400 mg/L in 250 mL of conical flask for a period of 4 hours which was sufficient to reach equilibrium time. Two generally used isotherm models, the Langmuir and Freundlich were selected to explain the dye and adsorbent from *C. equisetifolia* seeds interaction. In order to characterize the equilibrium data, the experiment data was fitted to adsorption isotherm models, and the best-fitted model was selected. Hence, the linear regression was used to determine the best fitted isotherm and the correlation coefficient was analyse in order to compare the applicability of the isotherm equations.

3.6.1 Langmuir equilibrium model

The Langmuir models indicates that the adsorption occurs until a monolayer of adsorption complete and consequently, there are no more interaction between the adsorbent and adsorbate molecules taking place (Mittal *et al*., 2009). For solid-liquid systems the linear form of the isotherm can be stated by the equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \left(\frac{1}{K_L . q_{max}}\right) \tag{3.3}$$

where,

C_e = concentration in the dye solution at equilibrium (mg/L);

q_e = solute adsorbed per unit mass of adsorbent at equilibrium (mg/g);

K_L = Langmuir constant (L/mg) which is related to the energy of adsorption; and

q_{max} = the theoretical maximum adsorption capacity (mg/g).

A graph of C_e/q_e versus C_e was plotted in order to express the q_{max} and K_L from the slope and intercept, respectively. From the value of K_L, the separation factor or equilibrium parameter, R_L was calculated using the equation:

$$R_L = \frac{1}{1+K_L C_0} \tag{3.4}$$

where,

C_0 = maximum initial concentration (mg/L); and

K_L = Langmuir constant (L/mg).

The R_L value of the Langmuir isotherm shows the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

3.6.2 Freundlich equilibrium model

The Freundlich adsorption isotherm proposes that adsorption takes place on heterogeneous surface having unequally available sites with different energies of adsorption and the isotherm can be expressed as equation:

$$loq\ q_e = \log K_f + \frac{1}{n} \log C_e \tag{3.5}$$

The intensity of the adsorption or the degree of nonlinearity between concentration of solution and amount adsorbed, n and Freundlich adsorption constant, K_f, for Freundlich isotherm were determined from the plot of $\log q_e$ and $\log C_e$. From the slope and intecept of the plot, the value of n and K_F can be calculated, respectively. If the value of n from the Freundlich equation is between 0 and 10 or the value of $1/n$ is less than 1, the adsorption is assumed to be favourable adsorption.

3.7 Kinetic studies

The adsorption of malachite green and neutral red dye on adsorbent from *C. equisetifolia* seeds were studied at different dye concentration which are from 200 to 400 mg/L. For computing the adsorption kinetics of both dyes, the pseudo-first-order and pseudo-second-order models were used to fit the experimental data. Besides that, parameters such as amount of dye adsorbed calculated from the plots, $q_{e,(calculated)}$ and rate constant, k were determined from the plots.

3.7.1 Pseudo-first-order kinetic model

Equation 3.6 represents pseudo-first-order rate equation:

$$log\ \left(q_e - q_t\right) = log\, q_e - \frac{k_1}{2.303} t \tag{3.6}$$

where,

q_e = the amount of dye adsorbed at equilibrium;

q_t = the amount of dye adsorbed at any time t; and

k_1 = the first-order rate constant (min^{-1})

The value of k_1 was determined from the slope of the plot between $log\ (q_e - q_t)$ versus time, t. The value of linear regression coefficient, R^2 was determined in order to indicate the best fitted data to the model. The calculated q_e value was calculated from the intercept of the kinetic model plots and the experimental q_e was selected from the batch experiment data. Then, the calculated q_e was compared with the experiment q_e value to demonstrate the adsorption follows the pseudo-first-order model.

3.7.2 Pseudo-second-order kinetic model

The adsorption data was evaluated in terms of pseudo-second-order mechanism which is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3.7}$$

where,

k_2 = the pseudo-second-order rate constant (g/mg.min).

A plot between t/q_t versus t was plotted and then the value of the constant k_2 and q_e were calculated from the plot. The regression coefficients, R^2 were determined from the plot in order to show the best fit data to the model. The calculated q_e value was compared with the experiment q_e value to demonstrate the adsorption follows the pseudo-second-order model.

3.8 Research Framework

Research framework was designed for a better understanding of this research. This framework provided overall methodology on the preparation and characterization of adsorbent from *C. equisetifolia* seeds for dye adsorption.

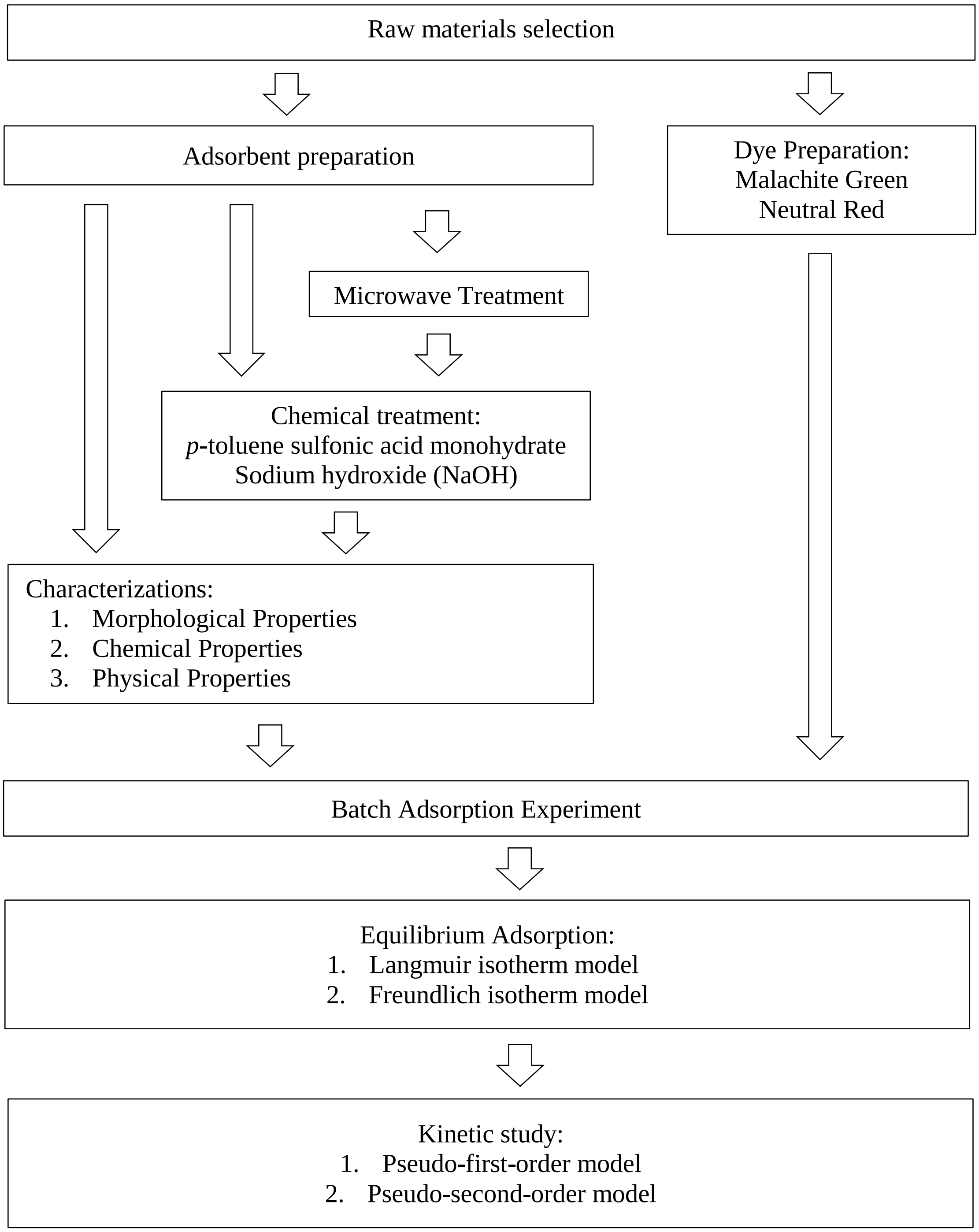


Figure 3.4: Research Framework

CHAPTER 4

RESULTS AND DISCUSSION

In order to achieve the aim of the research, several characterization studies were conducted to determine chemical, physical and morphological properties of the adsorbent from *C. equisetifolia* seeds. Moreover, the adsorption performance of the absorbent from *C. equisetifolia* seeds was studied by batch adsorption method. The experiments of batch adsorption studies were conducted and the results of all three adsorbents from *C. equisetifolia* were compared in order to identify the efficacy of the adsorbents. Furthermore, the adsorption of the dyes was further studied by Langmuir and Freundlich models. The adsorption kinetic models, pseudo-first and pseudo-second-order rate model have been established in order to understand the adsorption mechanisms of dyes and its potential rate-controlling steps.

4.1 Properties of *Casuarina equisetifolia* seeds

4.1.1 Chemical properties

The determination of chemical properties of an adsorbent is important in order to understand the required chemical characteristics of adsorbents from *C. equisetifolia seeds* for the removal of dyes. In this research, chemical composition and functional group of adsorbents from *C. equisetifolia* seeds were studied.

4.1.1.1 Chemical composition

The chemical compositions of *C. equisetifolia* seeds are summarized in Table 4.1. A few test was conducted to determine the percentage of moisture content, ethanol-toluene solubility, holocellulose content, alpha-cellulose content, lignin content, ash content, hot water solubility, NaOH solubility, and pentosan. The determination of ethanol-solubility, lignocellulose materials, hot water solubility, ash content and NaOH solubility are commonly applied in the characterization of adsorbent from agro-waste because these characteristics are important for the adsorption of dyes. The results show that all three adsorbent from *C. equisetifolia* seeds have a slightly different percentage of chemical compositions.

Table 4.1: The chemical composition of *C. equisetifolia* seeds

Properties	**Contents (%)**		
	Raw seeds	**Acid-alkali treated seeds**	**Microwave-acid-alkali treated seeds**
Moisture content	9.6	10.5	9.4
Ethanol-toluene solubility	3.0	2.7	2.4
Holocellulose content	60.7	57.0	56.0
Alpha-cellulose content	24.1	25.8	25.2
Hemicellulose content	36.6	31.2	30.8
Lignin content	45.2	50.0	50.2
Ash content	2.2	1.9	2.1
Hot water solubility	9.2	5.5	4.5
Alkali solubility	30.0	28.4	27.5
Pentosan	17.0	10.8	14.3

According to TAPPI standard, the ethanol-toluene solubility is accomplished to determine the quantity of extraneous materials such as waxes, fats, resins and certain other insoluble component, for example, gums (Zaki *et al.*, 2012). Microwave-acid-alkali treated seed gives the lowest percentage compared to acid-alkali treated and raw seeds which are 2.4%, 2.7%, and 3.0 % respectively. Consequently, hot water solubility has obviously decreased in all *C. equisetifolia* seeds adsorbents from 9.2% to 4.5%. The determination of hot water solubility are referred to the presence of material such as sugar, starch, tannins, gums and colouring matter that exist in wood. It could be concluded that the extraneous materials which known as non-polar constituent obtained from ethanol-toluene and hot water solubility were extracted during the modification by acid, alkali and microwave treatments. The extraction of the non-polar constituents is important in order to enhance the active surface percent of adsorbent and thus increase the adsorption efficiency (Argun & Dursun, 2006).

Holocellulose consists of alpha-cellulose and hemicellulose. It can be seen that the holocellulose contents for all three adsorbents were 60.7% for raw, 57.0% for acid-alkali treated and 56.0% for microwave-acid-alkali treated seeds. A similar percentage was observed in a study of chemical properties of juvenile latex timber clone rubber wood trees which are from 56.4% to 60.56% (Zaki *et al*., 2012). The alpha-cellulose contents of *C. equisetifolia* seeds were from 24.1% to 25.8%. Meanwhile, the hemicellulose contents were calculated from the holocelullose and alpha-cellulose contents. The percentage of hemicellulose were 36.6% for raw, 31.2% for acid-alkali treated, and 30.8% for microwave-acid-alkali treated seeds. A study from Argun *et al*. (2009) showed that the percentage of hemicellulose presents in the adsorbent from pine bark which are from 28.5% to 32.7% which are as higher as the percentage of hemicellulose of *C. equisetifolia* seeds.

After the modification of *C. equisetifolia* seeds by acid, alkali and microwave treatment, the lignin contents of *C. equisetifolia seeds* were increased from 45.2% to 50.2%. Previous researchers had proven that several adsorbents from lignocellulosic waste have high efficiency in the adsorption of dye (Zhou *et al*., 2013; Fathy *et al*., 2013; Sartape *et al*., 2014). The lignocellulosic matrix of plant-based represents a wide variety of functional groups that play a main part for binding dyes over different mechanisms. The adsorption generally takes place by complexation, ion exchange and hydrogen bonding (Djilali *et al*., 2012). Furthermore, the content of ash was also determined in the characterization of chemical properties of *C. equisetifolia* seeds. The ash content is related to the amount of mineral such silica (Mohmod *et al*., 1992). From the results, it showed that the ash content for raw and treated *C. equisetifolia* seeds were from 1.9% to 2.2%. The ash contents in *C. equisetifolia* seeds were almost similar to that of the activated carbon from coconut shell which from 1.37% to 1.55% (Devi *et al*., 2012). Previous researchers had been proven that lower values of ash content favour to good characteristics of adsorbents (Malik *et al*., 2015).

Besides, the determination of alkali solubility of *C. equisetifolia* seeds is also important in order to know the existence of compounds such as organic acid, polysaccharides, or tannin. From the results, the alkali solubility of raw, acid-alkali treated and microwave-acid-alkali treated seeds were 30.0%, 28.4% and 27.5%, respectively. A decreased percent of alkali solubility implied that the organic acid, polysaccharides and tannins from the seeds have been slightly extracted. The removal of these compounds was required because the phenolic group of polysaccharides and tannin can stain the water and increased the COD of water (Argun & Dursun, 2008).

4.1.1.2 Surface Functional Groups

Figure 4.1 shows FTIR spectra of three different adsorbents from *C. equisetifolia* seeds, i.e. raw, acid-alkali treated and microwave-acid-alkali treated seeds. The band at 3342 to 3325 cm^{-1} represented the O – H group stretch. This band was due to the hydroxyl group of adsorbed water on the *C. equisetifolia* seeds surface and polymeric compounds especially polysaccharides linked in cellulose (Fan *et al.*, 2012). The band at 2924.09 cm^{-1} for all three adsorbents was due to the stretching of C – H in carboxylic acid with their bending vibration observed at 1352.10 cm^{-1}, it indicates the presence of cellulose and hemicellulose group (Khattri and Singh, 2009).

On the other hand, peak at 1701.22, 1720.50 and 1714 cm^{-1} were assigned to the stretching of C = O of the uronic ester and acetyl groups of hemicellulose. Otherwise, the stretching also indicated the ester linkage of carboxylic group of the *p*-coumaric acids and ferulic of lignin (Bledzki *et al.*, 2010). Meanwhile, a peak at 1618.28 cm^{-1}, 1647.21 cm^{-1}, and 1616.35 cm^{-1} indicated the C = C bond. The band interval in between 1650-1500cm^{-1} represents the aromatic skeletal mode of lignin. A study onto the removal of Cd(II), Pb(II), Cu(II) and Ni(II) from water using modified pine bark also revealed similar results (Argun *et al.*, 2009). Meanwhile, the peaks at 1022.27 to 1026.13 cm^{-1} represented the vibration of C – O because of the ether group of the cellulose structure of the *C. equisetifolia* seeds. The vibration also proved from the adsorption study of an anionic dye, Tartrazine, from aqueous solutions onto agricultural by-product saw dust (Banerjee & Chattopadhyaya, 2013).

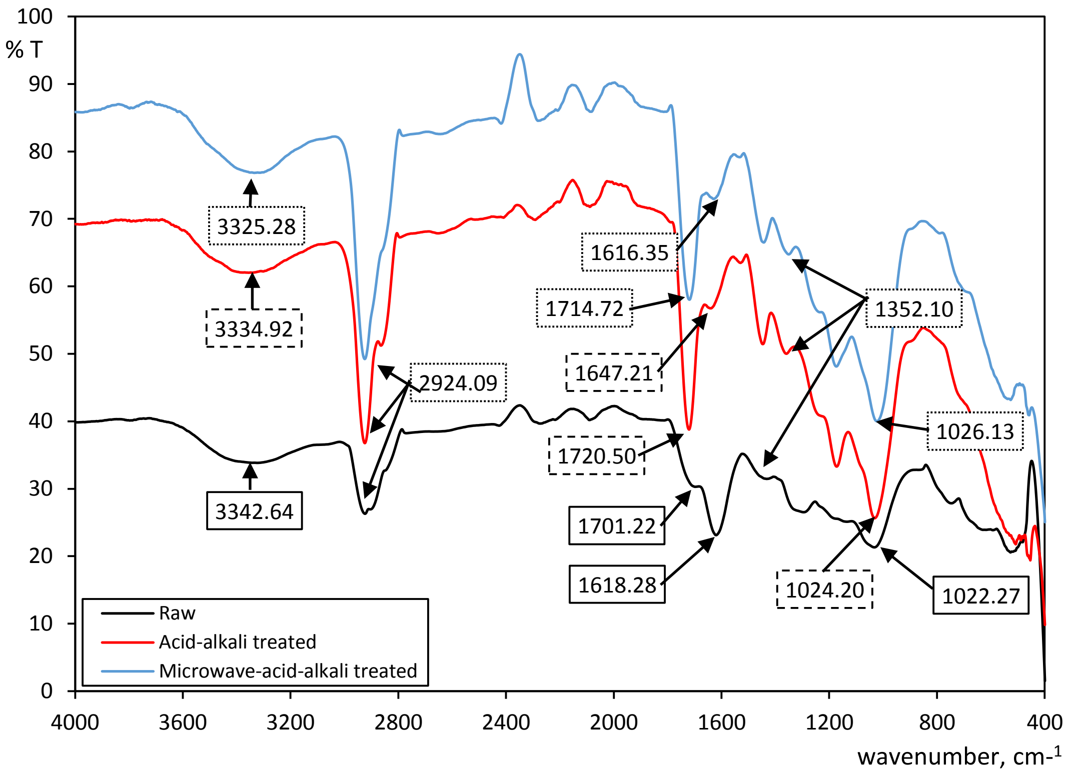
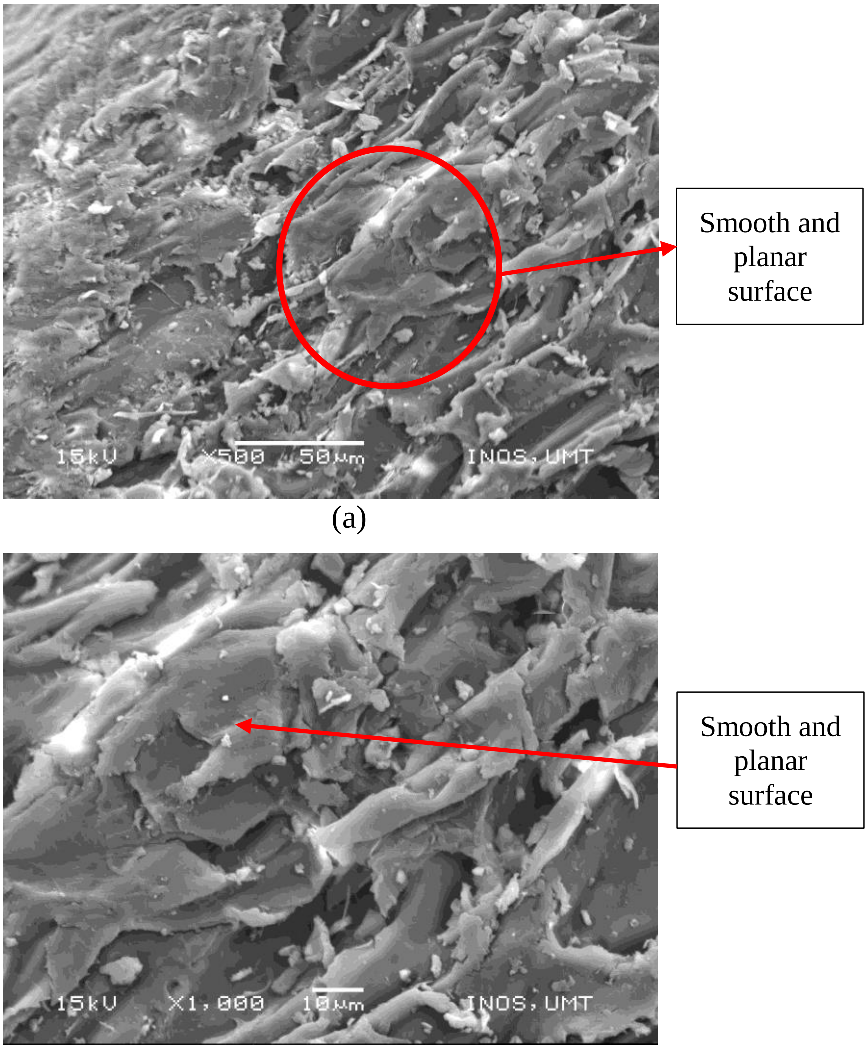


Figure 4.1: The FTIR spectra of raw, acid-alkali treated and microwave-acid-alkali treated *C. equisetifolia* seeds

FTIR spectra for all three adsorbents from *C. equisetifolia* seeds showed similar characteristics but with slight changes in peaks and differences in the intensity of the band. This is because there were different distribution of those functional groups exist in raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds. Otherwise, a strong band in between 3342 to 3325 cm^{-1} was indicated that all three adsorbents have the abundance of hydroxyl groups. It was shown that modification with acid-alkali and microwave-acid-alkali treatment brought an increase in vibration of C – H stretching at 2924.09 cm^{-1}, carboxyl groups C = O at 1701 to 1720 cm^{-1} and C – O bonds at 1022 to 1027 cm^{-1}. The shifting of the wave numbers for hydroxyl (3342 to 3325 cm^{-1}) and carboxyl (1701 to 1720 cm^{-1}) groups representing the possible contribution of these two groups in the modification of *C. equisetifolia* seeds. The shifting of those wave number were also presented in the FTIR study of coconut shell activated carbon (Mohammed *et al.*, 2015). Besides, the increase of hydroxyl and carboxyl groups might role as proton donors, therefore deprotonated hydroxyl and carboxyl groups may be encompassed in the adsorption of the positive dye ions (Han *et al.*, 2010).

4.1.2 Surface Morphology

The surface morphologies of adsorbent from *C. equisetifolia seeds* were analysed using scanning electron microscope (SEM). The SEM images for raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia seeds* show slightly different in the surface texture. There were changes in the surface of all adsorbents from *C. equisetifolia* seeds. Figure 4.2 shows the SEM images of surface morphology of raw *C. equisetifolia* seeds under the magnification of 500 and 1000 times. The surface of raw *C. equisetifolia* seeds was smooth and planar surface.

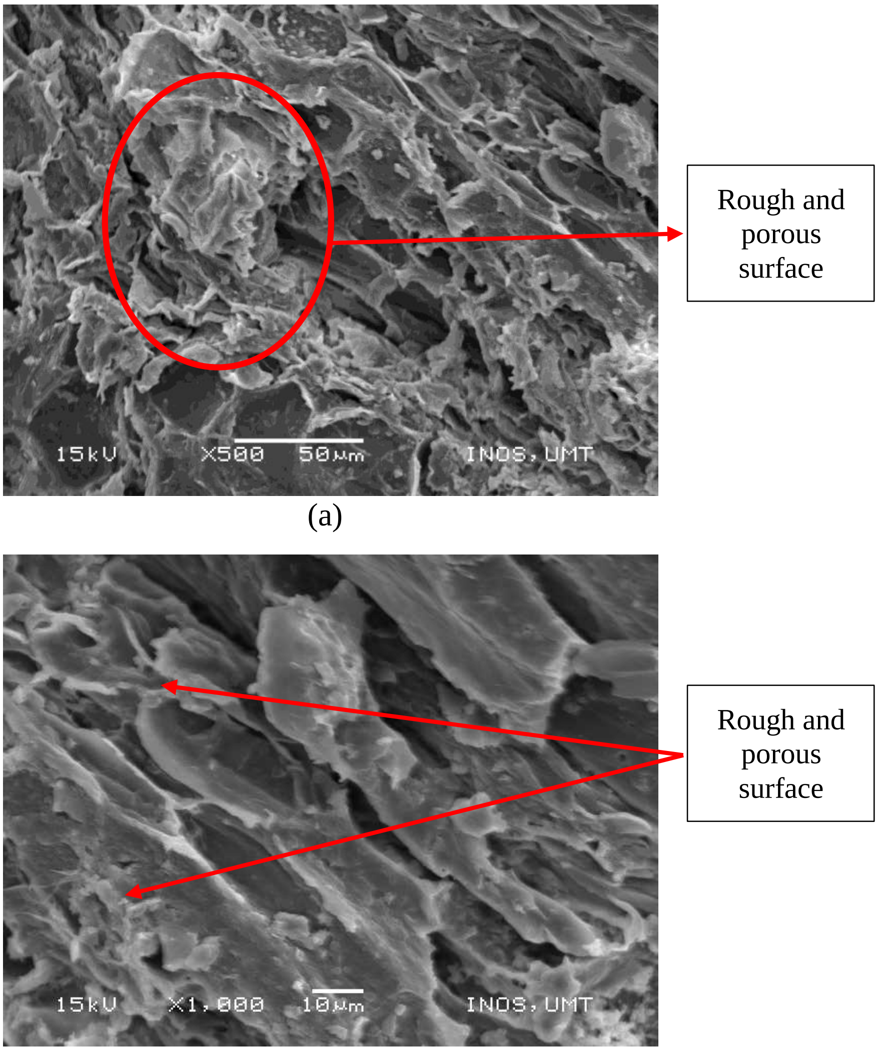


(a)

(b)

Figure 4.2: SEM images of raw *C. equisetifolia* seeds under (a) 500x and (b) 1000x magnification

Figure 4.3 shows the SEM images of surface morphology of acid-alkali treated *C. equisetifolia* seeds under the magnification of 500 and 1000 times. After the modification with acid and alkali solution, the development of heterogeneous and rough with porous cavities was shown on the surface of *C. equisetifolia* seeds. The structure of the adsorbent was altered because of the removal of silica, hemicellulose, and lignin from the interfibrillar region (Ciannamea *et al*., 2010). The obtained results were in agreement with Fathy *et al*. (2013) where it was found that the surface morphological of adsorbent from rice straw changed and altered into the rough and porous surface after alkali treatment. Therefore, it confirmed that acid and alkali treatment bring significant impact on morphological properties of cellulose thus can change in crystallinity, pore structure, stiffness, accessibility, orientation of fibrils and unit cell structure in cellulosic fibers (Chakraborty *et al*., 2011).

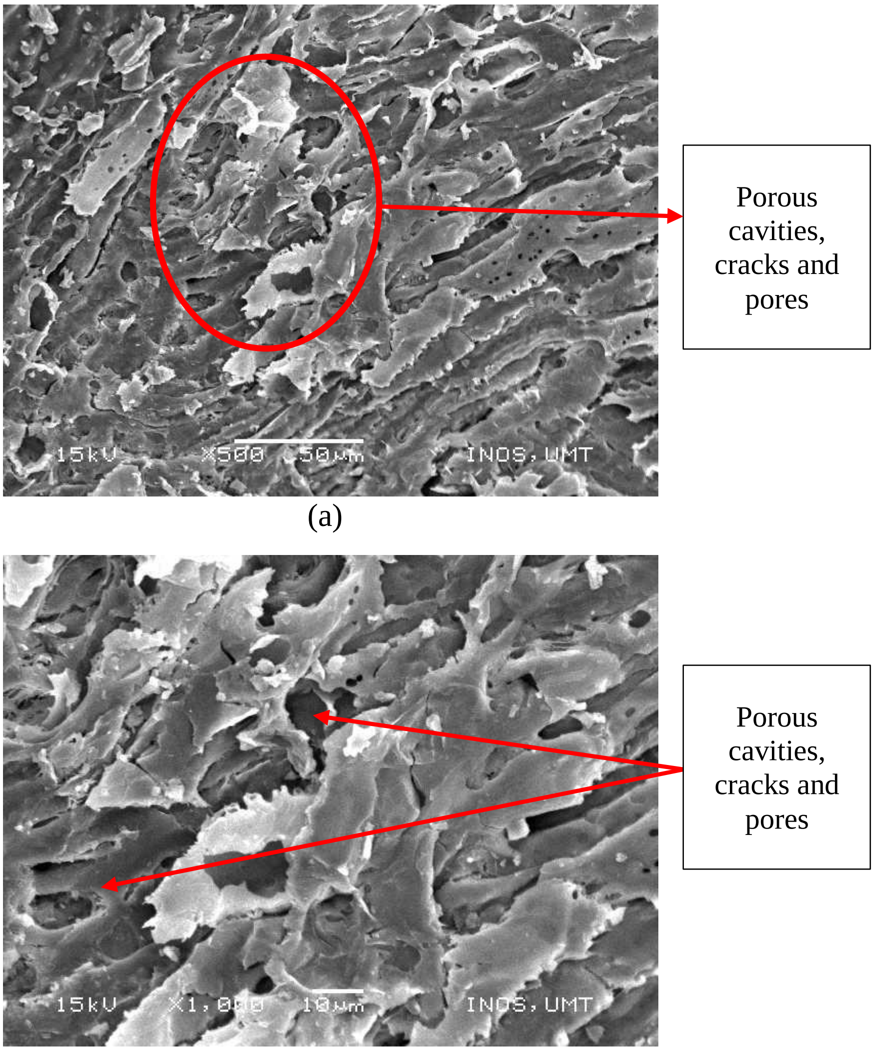


(b)

Figure 4.3: SEM images of acid-alkali treated *C. equisetifolia* seeds under (a) 500x and (b) 1000x magnification

SEM images of microwave-acid-alkali treated *C. equisetifolia* seeds under magnification of 500 and 1000 times are represented in Figure 4.4. It clearly shows an increase in surface roughness with highly porous cavities and cracks compared to raw.

In addition, compared to raw and acid-alkali treated seeds, the pores were introduced at the surface of microwave-acid-alkali treated seeds. The higher porosity and the development of pores on the surface of microwave-acid-alkali treated *C. equisetifolia* seeds may be contributed to the thermal decomposition of its organic substance or release of volatile gases from *C. equisetifolia* seeds during microwave treatment. Similar observations were observed in the study of physico-chemical and surface characterization of groundnut shell adsorbents (Malik *et al.*, 2006). Besides that, results by Maldhure and Ekhe (2011) proved that the same changes in the surface structure of the adsorbent from industrial waste lignin after the microwave treatment.



(a)

(b)

Figure 4.4: SEM images of microwave-acid-alkali treated *C. equisetifolia* seeds under (a) 500x and (b) 1000x magnification

4.1.3 Surface Charging

Surface charges of adsorbent from *C. equisetifolia* seeds were obtained from the zeta potential by using electro kinetic analyser (EKA). The determination of surface charges of adsorbent was important to identify the principle of the adsorbent surface and its surroundings interactions. From the Table 4.2, the zeta potentials of raw, acid-alkali and microwave-acid-alkali treated adsorbent from *C. equisetifolia* seeds were -19.594 mV, -21.199 mV and -20.977 mV, respectively. The results showed that the surface charges of all adsorbents are negative. These negative surface charges are associated with carboxyl and phenolic OH groups in the lignocellulosic materials of *C. equisetifolia seeds* (Magriotis *et al*., 2014). Hydroxyl ions (OH^-) contributed to negatively charge the adsorbent surface and promoted the adsorption of cationic dyes are adsorbed on the surface.

Table 4.2: The zeta potential *C. equisetifolia* seeds adsorbents

***Casuarina equisetifolia* plant seeds**	**Zeta Potential (mV)**
Raw	-19.594
Acid-alkali treated	-21.199
Microwave-acid-alkali treated	-20.977

4.1.4 Surface Area

BET surface area of *C. equisetifolia seeds* was found to be in the range of 0.4884 m^2/g to 0.8878 m^2/g. The values of surface area were lower compared to other lignocellulosic adsorbents, for example, 13 m^2/g for banana peel (Memon *et al*., 2008), 452 – 1590 m^2/g for avocado kernel seeds (Elizalde-Gonza´lez *et al*., 2007), 1976 –

2595 m^2/g for corncob (Tseng and Tseng, 2005), and 972 m^2/g for rambutan peel (Njoku *et al*., 2014). This low surface area is possibly due to the operational complexity involved in degassing the lignocellulosic samples. The determination of BET surface area of lignocellulosic waste is difficult because the powder is burnt even before reaching the degassing temperature. Degassing temperature for the preparation of a material for BET analysis is depended on the sample and basically the sample should be degassed at the highest temperature (up to 350°C) that will not cause a structure change to the sample. Thus, the degassing temperature (100°C) is reduced, which results in low surface area owning to the presence of moisture (Pathak & Mandavgane, 2015). Other authors have reported values of BET surface area for lignocellulosic waste between 0.65 m^2/g to 5 m^2/g which as lower as in this research (Palma *et al*., 2011; Pathak & Mandavgane, 2015; Sharma & Bhattacharyya, 2005).

4.2 Batch adsorption studies

These studies were carried out by shaking 250 mL of conical flasks containing a desired amount of adsorbent from *C. equisetifolia* seeds and 100 mL of dye solutions of preferred concentration on water shaker bath at 250 rpm at room temperature. The effects of different parameter in the batch adsorption experiment such as contact time, initial dye concentration, and adsorbent dosage were investigated.

4.2.1 Effects of contact time

One of the important variable in the adsorption studies is contact time because the data allows the confirmation on the length of agitation time to achieve equilibrium of the adsorption processes between the adsorbent and the adsorbates (Dahri *et al*., 2015). In this experiment, the effects of contact time (0 – 240 min) on the removal of malachite green by raw, acid-alkali treated and microwave-acid-alkali treated *C. equisetifolia seeds* were investigated at 200 mg/L of initial dye concentration of and 0.4 g of adsorbent dosage.

The results for the MG and NR dye removal are shown in Figure 4.5 and 4.6 respectively. Both adsorptions of MG and NR onto *C. equisetifolia seeds* adsorbents showed slightly similar trend whereby the percentage removal of both dyes sharply increased from 5 to 60 min and equilibrate beyond 150 min of contact time. The initial rapid increase in the percentage of dye removal is attributed to the abundance of active sites on *C. equisetifolia seeds* adsorbents and as time goes by these sites are saturated with the dyes and therefore, the adsorption slows down and finally unchanged (Mittal, 2006).

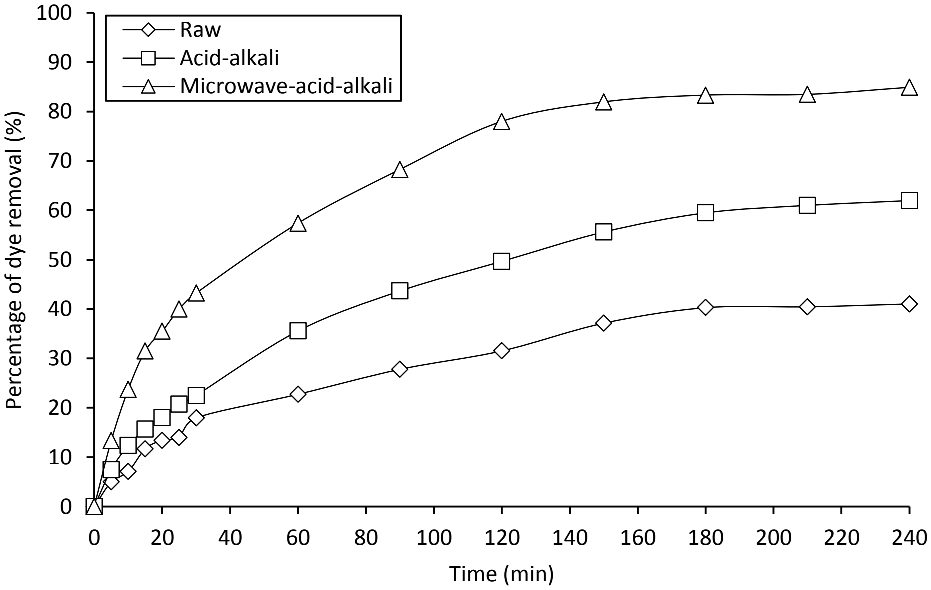


Figure 4.5: Effects of contact time on the removal of MG dye by *C. equisetifolia* seeds

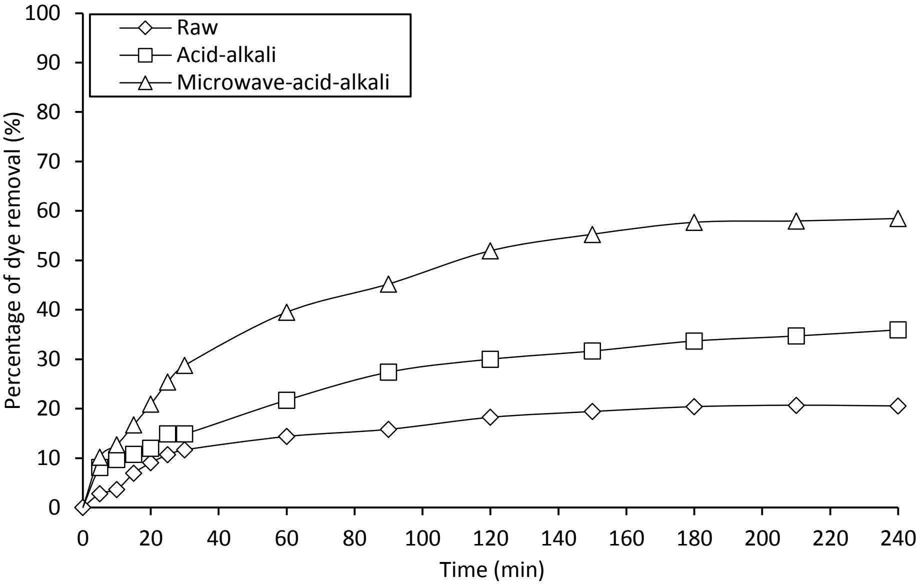


Figure 4.6: Effects of contact time on the removal of NR dye by *C. equisetifolia* seeds

The findings clearly indicated the adsorption of MG and NR dye on *C. equisetifolia seeds* followed three-step processes which are a rapid initial uptake, then a slower period of dye adsorption and lastly there is no significant adsorption take places. According to Mohammad *et al*. (2010), the first step is contributed to the bulk diffusion which is the instantaneous feeding of the most available sites on the surface of adsorbent. Then, pore diffusion or intra-particle diffusion has occurred which is the dye diffusion into the macropores from the adsorbent surface film. This step encouraged the further movement of the dye molecules from the liquid phase onto the surface of adsorbent. Finally, the last step is an equilibrium stage. In this stage, there was no significance changes in dye concentration was detected. The adsorption of the dye was suggested based on the observation of the curves shown in the Figure 4.5 to 4.6 which are smooth and continuous. Similar adsorption results were reported by Krishna and Swamy (2012) for calcined brick powder (PCB).

Based on the adsorption results of both dyes, the adsorption of MG dye onto adsorbent from *C. equisetifolia* seeds was recorded higher percentage compared to the adsorption of NR. The percentage of malachite green dye removal onto raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds were 41.05, 61.97 and 84.94 %, respectively, meanwhile, the percentage of NR onto raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds were 20.55, 35.93 and 58.44 %, respectively. The adsorption of MG dyes was higher compared to NR dye because NR dyes have lower molecular weight compared to MG dyes. According to Li *et al*. (2012), the adsorption capacity of activated carbon increases with the increase of adsorbate molecular weight.

4.2.2 Effects of initial dye concentration

In this study, a fixed quantity of the solute adsorbed by a given mass of adsorbent can be determined. When the initial concentration of dye was increased, the volume of dye that a given mass of adsorbent can adsorb was decreased because the fractional adsorption is low at high concentration range (Khattri & Singh, 2009). The experiments were conducted by shaking the adsorbent with 200, 300 and 400 mg/L concentration dye solution in conical flasks at room temperature in a water bath shaker.

4.2.2.1 Removal of malachite green (MG) dye

Figure 4.7, 4.8 and 4.9 present the results of MG dye removal onto raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds at different initial dye concentration, respectively. It can be seen that the percentage removal of MG decreased and the quantity of MG adsorbed per unit of adsorbent from *C. equisetifolia* seeds increased with the increase in initial dye concentration. The removal of dye was decreased from 41.0 to 21.0 %, 62.0 to 44.1 % and 85.0 to 51.4% with the increase in initial dye concentration from 200 to 400 mg/L for raw, acid-alkali and microwave-acid-alkali treated, respectively.

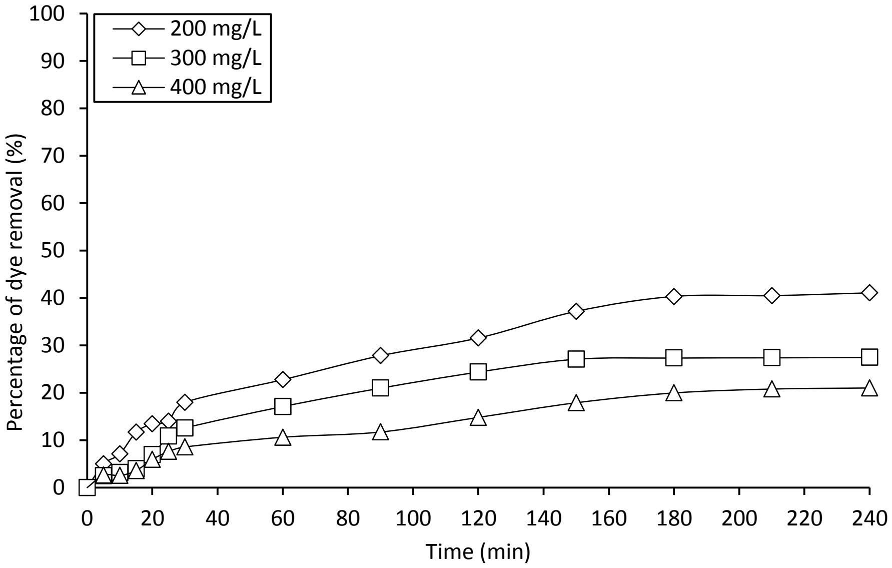


Figure 4.7: Effects of initial MG concentration on the percentage of MG removal onto raw *C. equisetifolia* seeds

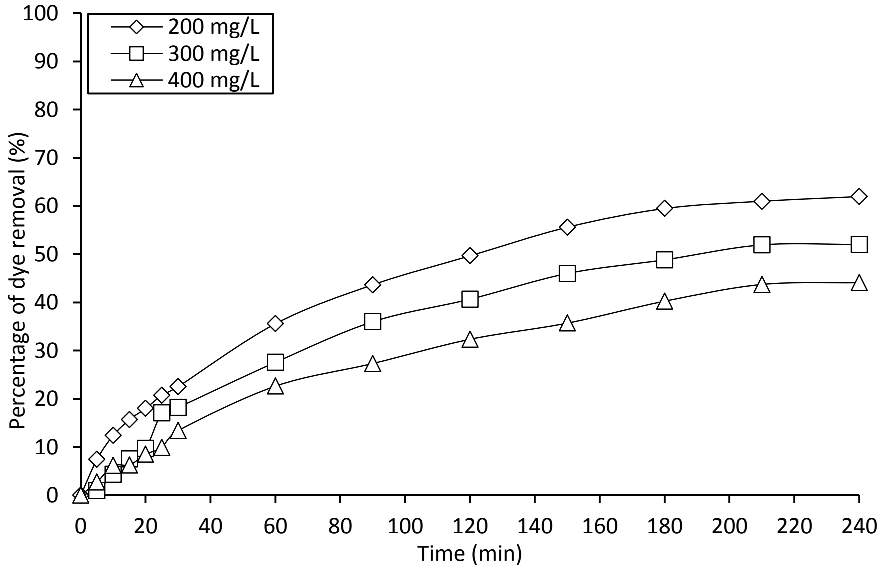


Figure 4.8: Effects of initial MG concentration on the percentage of MG removal onto acid-alkali treated *C. equisetifolia* seeds

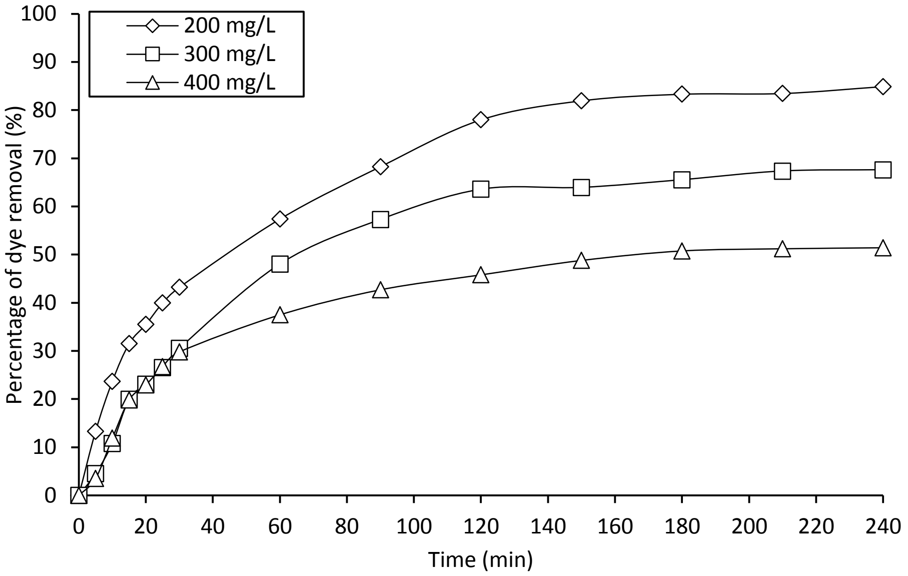


Figure 4.9: Effects of initial MG concentration on the percentage of MG removal onto microwave-acid-alkali treated *C. equisetifolia* seeds

From Table 4.3, the adsorption capacity, q_e of raw, acid-alkali and microwave-acid-alkali treated seeds increased from 20.57 to 21.39 mg.g^{-1}, 31.20 to 44.73 mg.g^{-1} and 42.36 to 51.33 mg.g^{-1}, respectively when initial dye concentration increased from 200 to 400 mg/L. This is because the higher concentration of dye can improve the interaction of the dye and adsorbent as well as provide driving force to cope with the resistance to mass transfer of dye (Sartape *et al*., 2013). All three adsorbents from *C. equisetifolia* seeds took about 180 min to remove MG dye before reaching equilibrium.

Table 4.3: The amount of MG dye adsorbed with dye concentration

Adsorbent	**Concentration of dye (mg/L)**	**Amount of MG absorbed, q_e (mg/g)**
Raw seed	200	20.570
	300	21.150
	400	21.385
Acid-alkali treated seed	200	31.198
	300	39.430
	400	44.730
Microwave-acid-alkali seed	200	42.363
	300	52.330
	400	51.710

4.2.2.2 Removal of neutral red (NR) dye

According to Figure 4.10, 4.11 and 4.12, the percentage of NR dye removal increased by the decrease in initial dye concentration and the equilibrium was attained within 180 min. It shows that the percentage of NR dye removal has a similar trend with the removal of MG dye. It was established that increasing the concentration from 200 to 400 mg/L leads to a decline in the percentage of removal from 20.55 to 11.88%, 35.93 to 21.71% and 58.44 to 36.60% for raw, acid-alkali treated and microwave-acid-alkali treated *C. equisetifolia* seeds, respectively. This is because the binding sites on the adsorbent found to be saturated and rapid exhausted as the number of dye molecules per unit volume increased (Rodríguez *et al.*, 2009).

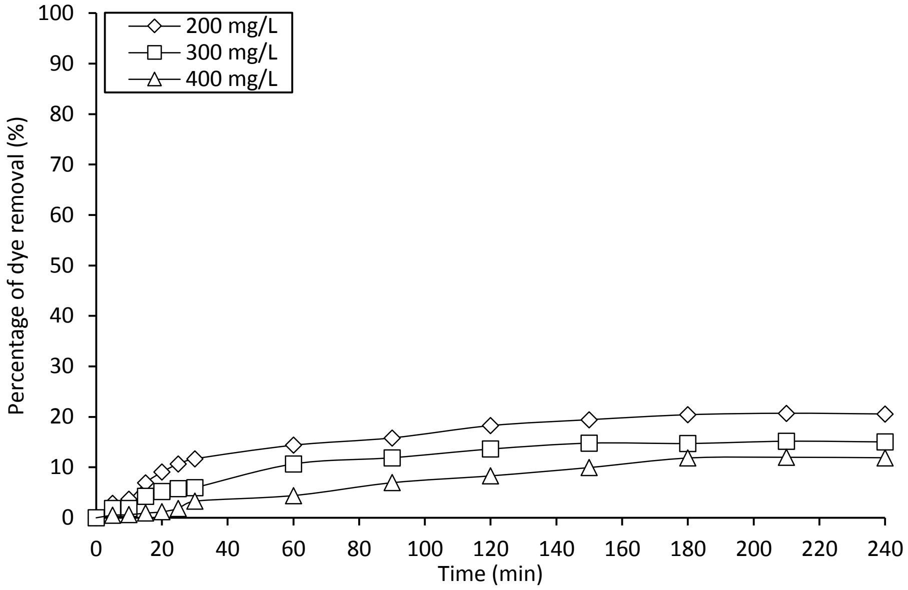


Figure 4.10: Effects of initial NR concentration on the percentage of NR removal onto raw *C. equisetifolia* seeds

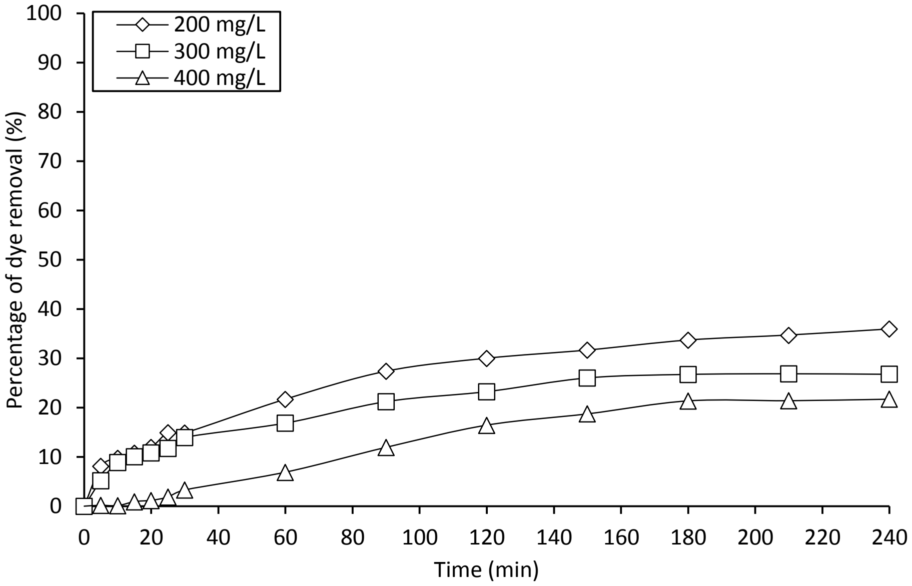


Figure 4.11: Effects of initial NR concentration on the percentage of NR removal onto acid-alkali treated *C. equisetifolia* seeds

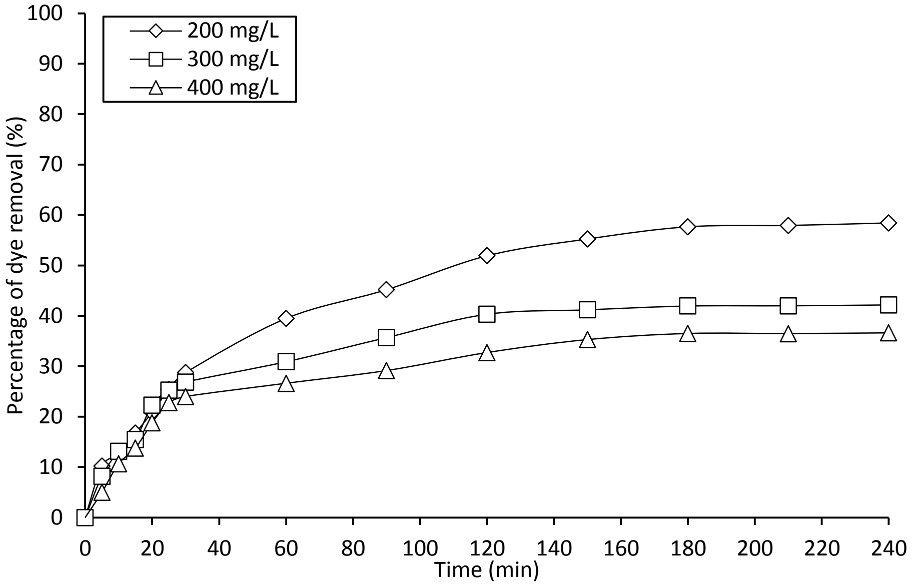


Figure 4.12: Effects of initial NR concentration on the percentage of NR removal onto microwave-acid-alkali treated *C. equisetifolia* seeds

Table 4.4 shows the amount of NR dye adsorbed by adsorbent from raw, acid-alkali treated and microwave-acid-alkali treated *C. equisetifolia seeds* increased from 10.38 to 11.89, 17.95 to 21.72 and 29.53 to 37.41 mg/g, respectively. The q_e increased with the increase of initial NR dye concentration due to increasing in driving force (Shahryari *et al*. 2010). From the findings, it was found that the removal of NR dye depends on upon the initial dye concentration. This is because the initial concentration provides the essential driving force to overcome the mass-transfer resistance between aqueous and solid phases on the adsorbent surface (Pathak and Mandavgane, 2015). Zhou *et al*., (2011) had studied about the removal of NR dyes onto spent cotton seed hull and the trend of the results was similar with this study. It showed that the ratio removal of NR decreases when the initial concentration increases from 250 to 500 mg/L.

Table 4.4: The amount of NR dye adsorbed with the dye concentration.

Adsorbent	Concentration of dye (mg/L)	Amount of NR adsorbed, q_e (mg/g)
Raw seed	200	10.375
	300	11.465
	400	11.885
Acid-alkali treated seed	200	17.953
	300	20.575
	400	21.718
Microwave-acid-alkali seed	200	29.530
	300	32.430
	400	37.410

According to the results, it clearly showed that microwave-acid-alkali treated *C. equisetifolia seeds* exhibited the highest percentage of MG and NR dye removal as well as the highest amount of MG and NR dye adsorbed. This is due to their characteristics which promoted binding more dyes on their surface. The presence of high lignocellulosic compound such as cellulose, hemicellulose and lignin as well as the chemical functional group such as C – H stretch, C = O groups and C – O bonds in the adsorbents from microwave-acid-alkali *C. equisetifolia seeds* have led the dyes to be adsorbed efficiency. On the other hand, the course and rough surface morphology, and also the negative surface charges of microwave-acid-alkali treated *C. equisetifolia seeds* has promoted adsorption of the cationic dyes to be adsorbed on the adsorbent surface.

4.2.3 Effects of adsorbent dosage

The adsorbent dosage is a parameter that gives an idea of the efficacy of an adsorbent and the ability of a dye to be adsorbed with a fixed dosage, so as to identify the ability of a dye from an economical point of view (Salleh *et al.*, 2011). In this experiment, 100 mL of dye solution (200 mg/L) was shake with different dosages (0.2 – 1.0 g) of the adsorbent in a water bath shaker at room temperature for 4 hours. This 4 hour period is appropriate time to achieve equilibrium at a constant agitation speed of 125 rpm.

4.2.3.1 Removal of malachite green (MG) dye

The effect of adsorbent dosage on the removal of MG dye on the raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia seeds* are shown in Figure 4.13, 4.14 and 4.15, respectively. The adsorption of MG dye for all three adsorbents show an increasing trend with the increasing adsorbent dosage from 0.2 g to 1.0 g. It is obvious that the removal percentage of MG dye for raw *C. equisetifolia seeds* was increased from 23.53 to 78.69%, for acid-alkali treated *C. equisetifolia seeds* was increased from 45.04 to 92.54% and for microwave-acid-alkali treated *C. equisetifolia seeds* was increased from 78.08 to 95.96%, with the increasing amount of adsorbent dosage from 0.2 to 1.0 g. The increasing dye removal percentage is due to the introduction of more binding sites with addition of more adsorbent dosage and adsorbent conglomeration (El-Bindary *et al.*, 2014). According to Table 4.5, the adsorption capacity of MG dye, q_e decreased when the adsorbent dosage increased because of the concentration gradient or splitting effect of the flux between dye concentration on the surface of the adsorbent and dye concentration in the solution. Same observations were reported in other study by Vadivelan & Kumar (2005) and Kumar *et al*. (2010).

Table 4.5: The amount of MG dye adsorbed with adsorbent dosage.

Adsorbent	**Adsorbent dosage (g)**	**Amount of MG adsorbed, q_e (mg/g)**
Raw seed	0.2	23.61
	0.4	20.57
	0.6	17.66
	0.8	16.85
	1.0	15.88
Acid-alkali treated seed	0.2	45.08
	0.4	31.20
	0.6	23.13
	0.8	21.06
	1.0	18.59
Microwave-acid-alkali seed	0.2	78.08
	0.4	42.36
	0.6	29.45
	0.8	23.30
	1.0	19.19

The highest percentage of MG dye removal for all adsorbents were achieved at 1.0 g for every 100 mL of dye solution which are 78.69% (raw seeds), 92.54% (acid-alkali treated seeds) and 95.96% (microwave-acid-alkali treated seeds). Meanwhile, the maximum amount of MG dye adsorbed was also achieved at 0.2 g for every 100 mL of dye solution which are 23.61, 45.08 and 78.08 mg.g^{-1} for raw, acid-alkali treated and microwave-acid-alkali treated *C. equisetifolia* seeds, respectively. The percentage of MG dye removal and the capacity of dye adsorbed for microwave-acid-alkali treated seeds was the highest compared to raw and acid-alkali treated seeds. This is associated to the surface morphology of microwave-acid-alkali treated seeds which is rough with porous cavities along with the negative surface charge as well as hydroxyl and carboxyl surface functional group on the adsorbent. Thus, allowing absorption of more dyes.

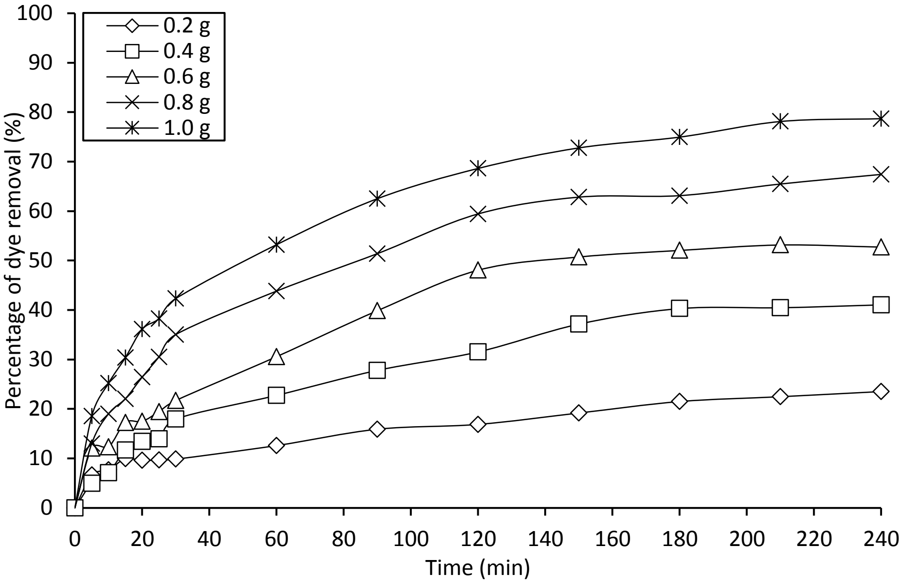


Figure 4.13: Effects of adsorbent dosage on the percentage of MG removal onto raw *C. equisetifolia* plant seeds

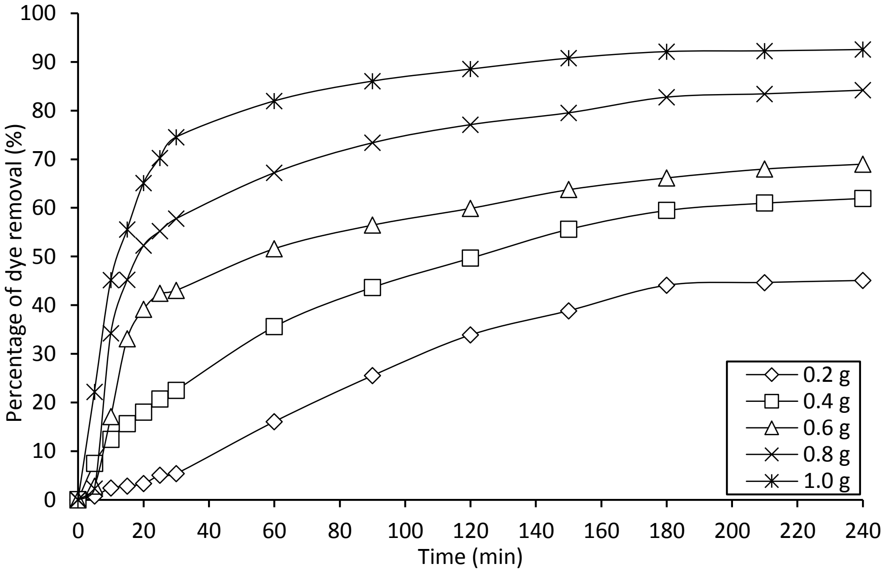


Figure 4.14: Effects of adsorbent dosage on the percentage of MG removal onto acid-alkali treated *Casuarina equisetifolia* plant seeds

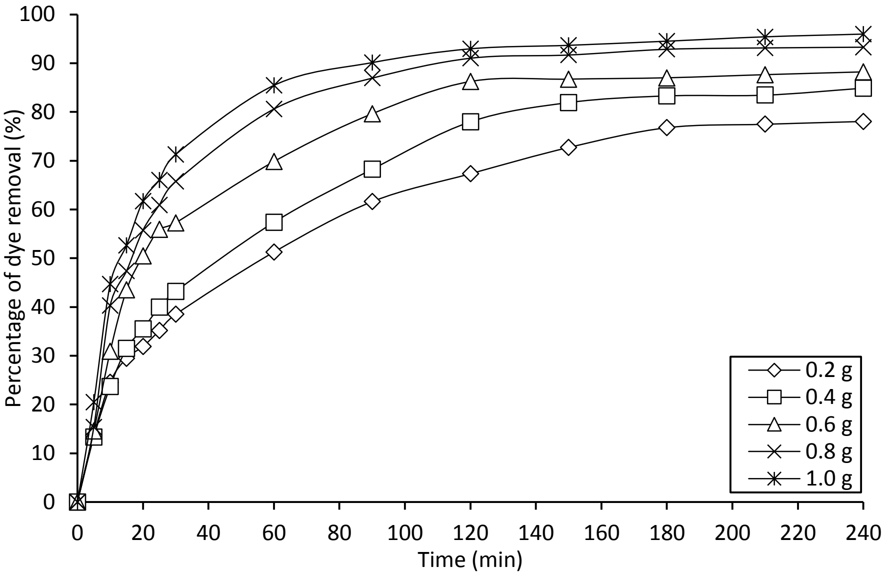


Figure 4.15: Effects of adsorbent dosage on the percentage of MG removal onto microwave-acid-alkali treated *C. equisetifolia* seeds

4.2.3.2 Removal of neutral red (NR) dye

Figure 4.16, 4.17 and 4.18 show the percentage of NR dye removal for raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds, respectively. The effect of adsorbent dosage for removal of NR showed a similar trend to the removal of MG. The results show that the increase in adsorbent dosage from 0.2 to 1.0 g resulted in an increase in the percentage removal of NR from 14.46 to 56.63%, 25.67 to 76.23% and 42.31 to 97.24% for raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds, respectively. This is due to the increase of surface area, thus more binding sites available causing the higher percentage of the NR removal (El-Bindary *et al.*, 2014).

Moreover, it was found in Table 4.6 that at equilibrium the amount of NR dye adsorbed at equilibrium was decreased with the increase in adsorbent dosage from 0.2 to 1.0 g which is from 14.58 to 11.27 mg.g^{-1}, 23.88 to 15.23 mg.g^{-1} and 42.34 to 19.65 mg.g^{-1} for raw, acid-alkali treated and microwave-acid-alkali treated *C. equisetifolia* plant seeds, respectively. The decrease of the amount of NR adsorbed at equilibrium by increasing adsorbent dosage is mostly due to the adsorption sites on the adsorbent remaining unsaturated during the adsorption process. This is because the increase in the adsorbent dosage might cause aggregation of adsorbent, and consequently, the available adsorption sites might decrease (Patil & Shrivastava, 2010).

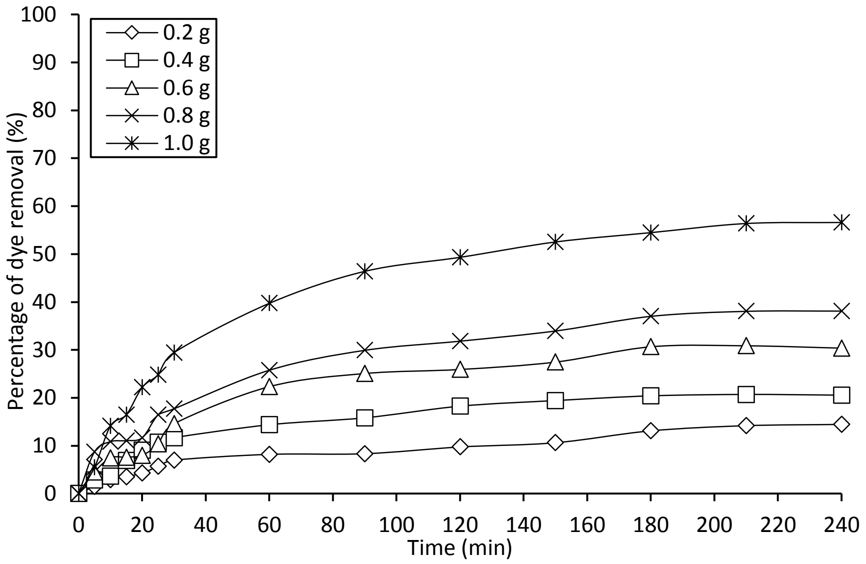


Figure 4.16: Effects of adsorbent dosage on the percentage of NR removal onto raw *C. equisetifolia* seeds

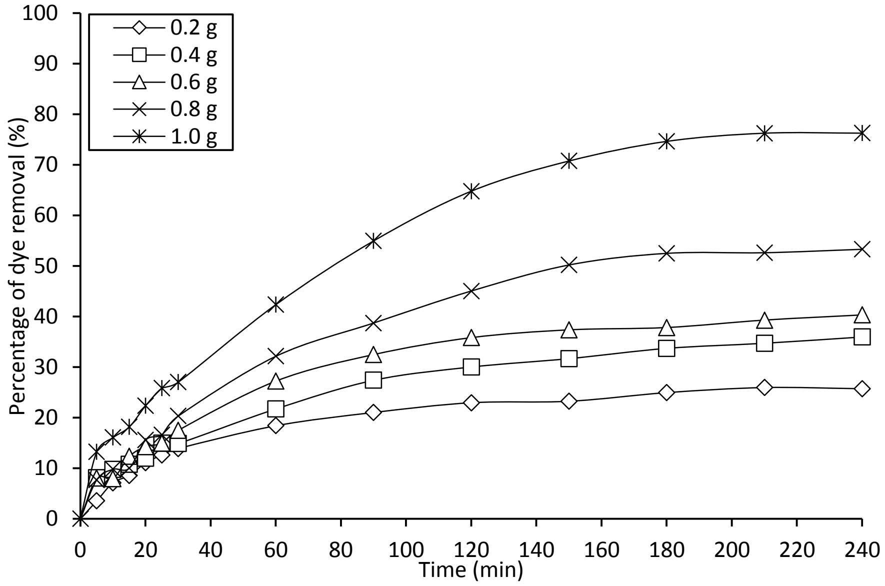


Figure 4.17: Effects of adsorbent dosage on the percentage of NR removal onto acid-alkali treated *C. equisetifolia* seeds

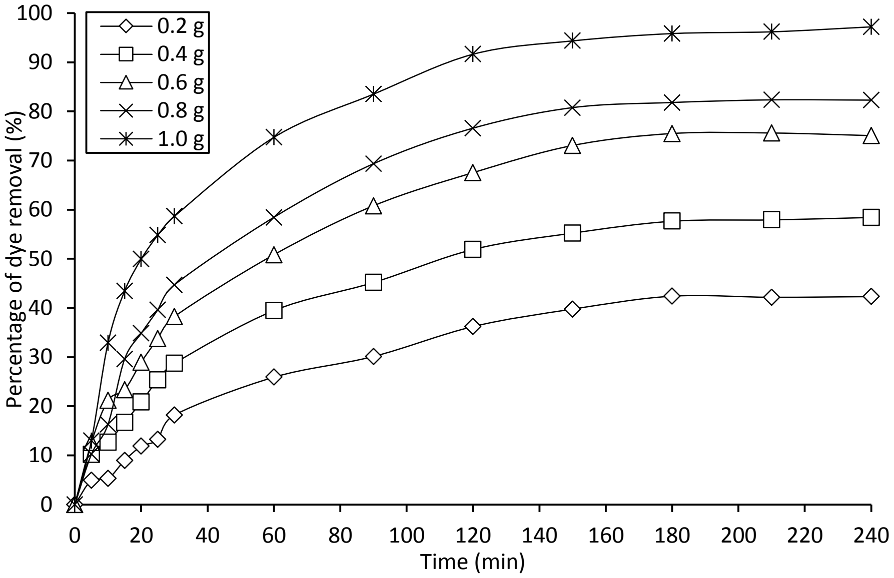


Figure 4.18: Effects of adsorbent dosage on the percentage of NR removal onto microwave-acid-alkali treated *C. equisetifolia* seeds

Table 4.6: The amount of NR dye adsorbed with adsorbent dosage.

Adsorbent	**Adsorbent dosage (g)**	**Amount of NR adsorbed, q_e (mg/g)**
Raw seed	0.2	14.58
	0.4	10.37
	0.6	10.12
	0.8	9.54
	1.0	11.27
Acid-alkali treated seed	0.2	23.88
	0.4	17.95
	0.6	13.41
	0.8	13.42
	1.0	15.23
Microwave-acid-alkali seed	0.2	42.34
	0.4	29.53
	0.6	25.06
	0.8	20.75
	1.0	19.65

Based in the finding from of batch adsorption analysis, it was found that the adsorption of MG and NR dye depended on the type of treatment on adsorbent. Different treatment determined different chemical distribution on adsorbent and modified morphological characteristics of the adsorbents. Microwave-acid-alkali treated *C. equisetifolia* seeds exhibited the best adsorption performance as compared to acid-alkali treated and raw *C. equisetifolia* seeds. The adsorption of dyes onto microwave-acid-alkali treated seeds were the highest due to the existence of required chemical composition and surface functional group along with well-developed surface morphology on the *C. equisetifolia* seeds.

4.3 Adsorption equilibrium studies

4.3.1 Langmuir equilibrium model

Langmuir model assumes the development of monolayer adsorbate on the outside of adsorbent, with adsorption can only happen at a fixed number of identical, equivalent and definite localised sites with no further adsorption takes place (Dada *et al.*, 2012; Foo & Hameed, 2010). The monolayer capacity can be signified as the known linear form of Langmuir equation,

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{4.1}$$

Langmuir plots of C_e/q_e vs. C_e for adsorption of MG and NR on all three adsorbent from *C. equisetifolia* seeds are shown in Figure 4.19 and 4.20, respectively. From the results, the plots provide a straight line of slope $1/q_{max}$ and the intercept $1/(q_{max}.K_L)$.

The Langmuir parameter for the adsorption of MG and NR onto *C. equisetifolia* seeds are listed in Table 4.7 and 4.8.

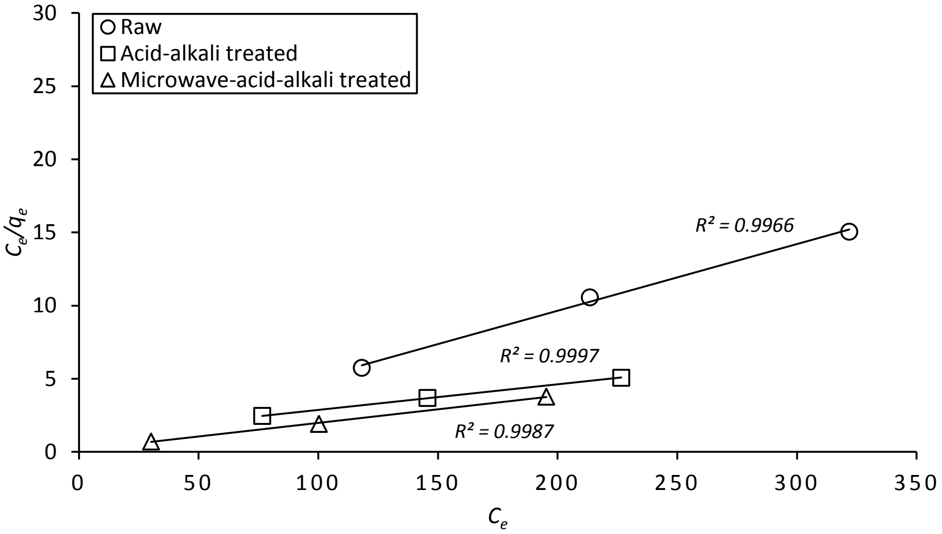


Figure 4.19: Langmuir plot for the adsorption of MG onto *C. equisetifolia* seeds

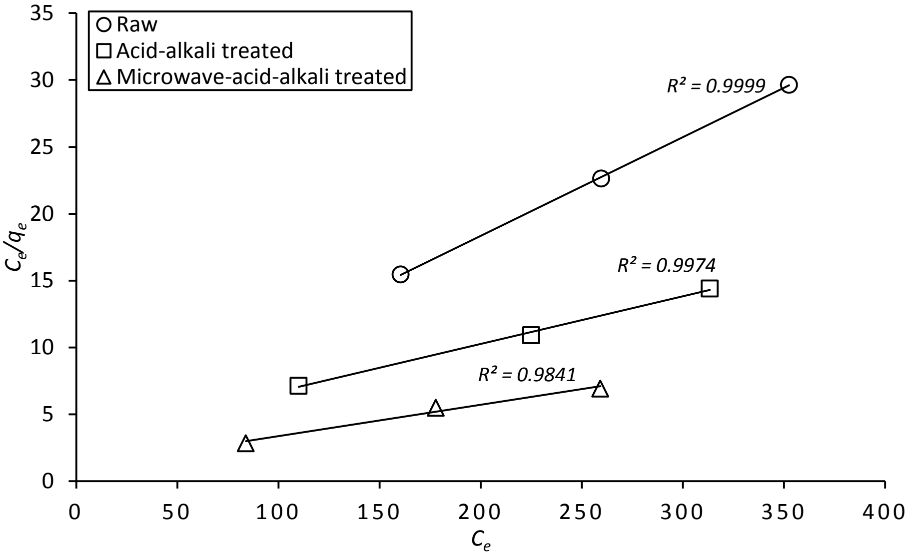


Figure 4.20: Langmuir plot for the adsorption of NR onto *C. equisetifolia* seeds

Table 4.7: The Langmuir parameter of malachite green onto *C. equisetifolia* seeds

***C. equisetifolia* seeds**	**Langmuir parameter**			
	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2
Raw	21.9298	0.0872	0.0279	0.9966
Acid-alkali treated	57.4713	0.0153	0.1403	0.9997
Microwave-acid-alkali treated	53.7634	0.1640	0.0150	0.9987

Table 4.8: The Langmuir parameter of neutral red onto *C. equisetifolia* seeds

***C. equisetifolia* seeds**	**Langmuir parameter**			
	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2
Raw	13.5318	0.0207	0.1075	0.9990
Acid-alkali treated	28.0112	0.0115	0.1787	0.9979
Microwave-acid-alkali treated	42.7350	0.0230	0.0979	0.9841

The results show that the adsorption process of MG and NR dye could be defined well with Langmuir isotherm. The experimental equilibrium data was fitted well to the equation with correlation coefficient values (R^2) greater than 0.98. The maximum monolayer coverage capacity (q_{max}) from the Langmuir isotherm model of MG dye were determined to be 21.930 , 57.471 and 53.763 mg.g^{-1}, meanwhile, q_{max} of NR dye were 13.532, 28.011 and 42.735 mg.g^{-1} which are for raw, acid-alkali treated and microwave-acid-alkali treated seeds, respectively. From the results, acid-alkali and microwave-alkali treated *C. equisetifolia* seeds have greater capacity of adsorption for the uptake of both dyes compared to the raw *C. equisetifolia* seeds.

The Langmuir isotherm constant, K_L for the adsorption of MG dye onto raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds were 0.087, 0.015 and 0.164 $L.mg^{-1}$, respectively, meanwhile the K_L for the adsorption of NR dye onto raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds were 0.021, 0.012 and 0.023 $L.mg^{-1}$ for, respectively. The values of K_L are associated with the values of q_{max}, where the lower K_L value is the greater q_{max} value. From the results, it show that the values of K_L for acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds were lower as compared to the raw *C. equisetifolia* seeds. The increasing value of q_{max} and decreasing of K_L was caused by the chemical, physical and morphological properties of the adsorbent as well as the interactions between the dyes and adsorbents from *C. equisetifolia* seeds (Kong *et al*., 2013).

The equilibrium parameter, R_L, is an important features denoted as separation factor or equilibrium parameter which is a dimensionless constant. From the data calculated in Table 4.3 and 4.4, the values of R_L for the adsorption of MG and NR dye on adsorbents from *C. equisetifolia* seeds are from 0.01 to 0.12. The values are greater than 0 but less than 1 in which indicate that Langmuir isotherm is favourable onto adsorbents from *C. equisetifolia* seeds under the experimental conditions used in this study.

4.3.2 Freundlich equilibrium model

The Freundlich isotherm model is assumed that the adsorption happens on the heterogeneous surface at sites which affected by the existence of different functional groups on the surface and interaction between adsorbent-adsorbate (El-Bindary *et al*., 2014; Fathy *et al*., 2013). The linear form of this model is expressed as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{4.2}$$

From the experimental results, the graphs of *log* q_e against *log* C_e for the uptake of malachite green and neutral red dye onto the adsorbents from *C. equisetifolia* seeds (Figure 4.21 and 4.22) were employed to produce the intercept value of K_f and the slope of *1/n*.

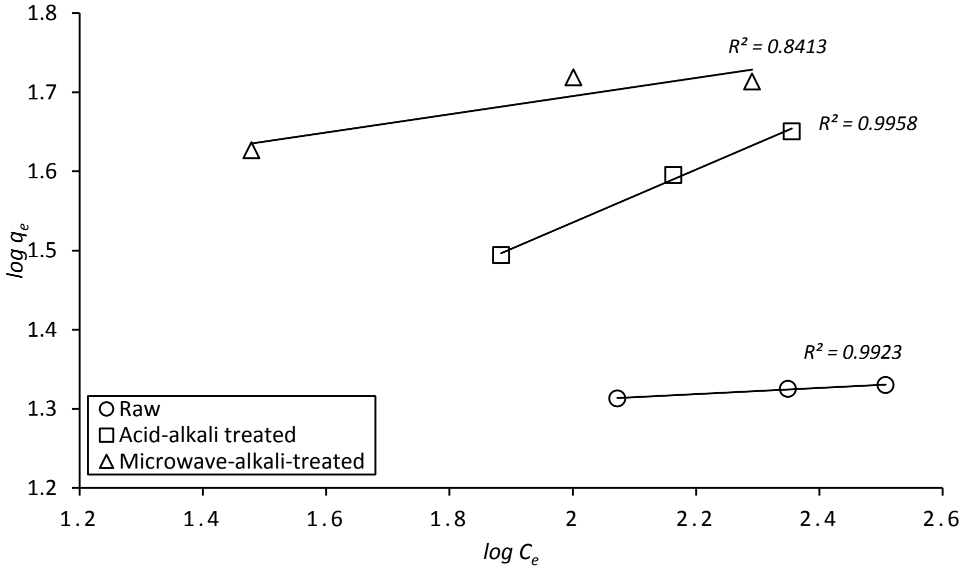


Figure 4.21: Freundlich plot for the adsorption of MG onto *C. equisetifolia* seeds

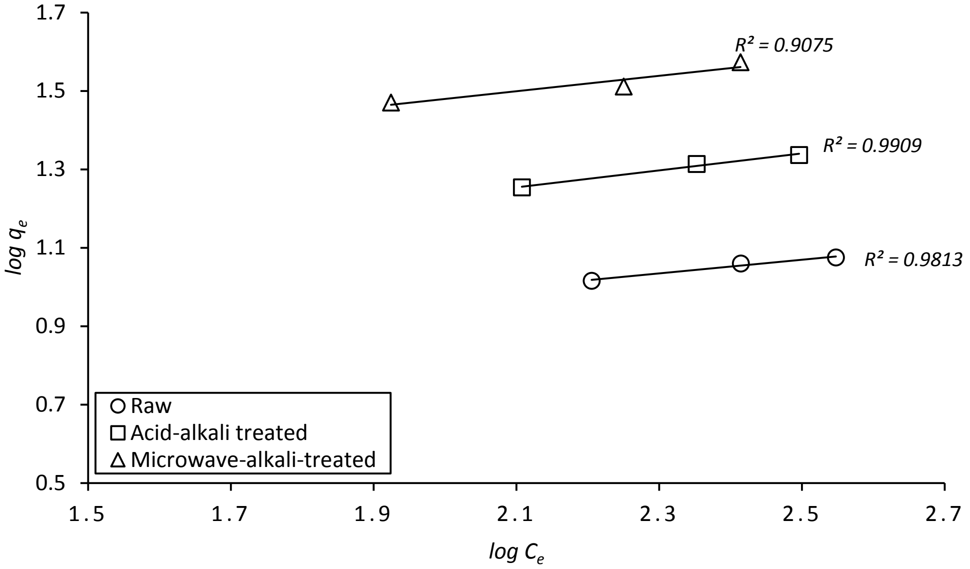


Figure 4.22: Freundlich plot for the adsorption of NR onto *C. equisetifolia* seeds

Figure 4.21 and 4.22 give marks on Freundlich isotherm fittings with linear regression coefficient (R^2) values greater than 0.84 and 0.99 for the MG and NR adsorption onto *C. equisetifolia* seeds, respectively. The Freundlich constant, K_f for the adsorption of MG onto raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds were 1.052, 1.049 and 1.317 mg.g^{-1}, respectively, meanwhile, for the adsorption of NR dye were 1.015, 1.026 and 1.064 mg.g^{-1}, respectively. The values of K_f show an increase from raw, acid-alkali treated seeds to microwave-acid-alkali treated seeds. It can be concluded that the acid-alkali and microwave-acid-alkali treated *C. equisetifolia seeds* have greatest adsorption capacity due to their increasing of K_f values (Vimonses *et al*., 2009).

Another Freundlich constant, *n* were defined from the slope of the plots that give the ideas about the favourability of the adsorption process. If the value of *1/n* is between 0 and 1, then the adsorbent surface is heterogeneous which is the intensity of adsorption is higher. However, if the value *1/n* is close to 0, the adsorbent surface is considered more heterogeneous (Pathak & Mandavgane, 2015). From Table 4.9 and 4.10, the values of *1/n* for the MG and NR adsorption onto the adsorbents from *C. equisetifolia* seeds lied in between 0 and 1, representing favourable adsorption. Meanwhile, the value of *n* was found to be in between 1.26 to 2.29. The values of *n* are larger than 1 which attributed to the dissemination of surface sites or any factor that causes a reduction of the interaction between adsorbent and adsorbate by increasing surface density. Besides, the values of *n* in the range of 1 to 10 indicate that the adsorption was good (Desta, 2013; Mckay & Oyrwsurn, 1980; Ozer & Pirinc, 2006).

Table 4.9: The Freundlich parameter of MG onto *C. equisetifolia* seeds

***C. equisetifolia* seeds**	**Freundlich parameter**			
	K_F (mg/g)	$1/n$	n	R^2
Raw	17.0648	0.0393	25.4453	0.9923
Acid-alkali treated	7.3536	0.3344	2.9904	0.9958
Microwave-acid-alkali treated	29.1944	0.1149	8.7032	0.8413

Table 4.10: The Freundlich parameter of NR onto *C. equisetifolia* seeds

***C. equisetifolia* seeds**	**Freundlich parameter**			
	K_F (mg/g)	$1/n$	n	R^2
Raw	4.2678	0.1780	5.6180	0.9813
Acid-alkali treated	6.3212	0.2159	4.6318	0.9909
Microwave-acid-alkali treated	12.1255	0.1978	5.0556	0.9075

According to isotherms studies, the results found are well fitted in the linear forms of Langmuir adsorption isotherm with R^2 of 0.984 to 0.999. The R_L value in the study were less than 1 which show that the adsorption of the MG and NR dyes onto adsorbents from *C. equisetifolia* seeds are favourable. Therefore, the adsorption of MG and NR dyes was expected to occur at specific homogeneous sites within the adsorbents from *C. equisetifolia* seeds. Besides that, there is a definite saturation limit and actively number of equivalent adsorption sites at which one molecules of the dye may be adsorbed on the surface of the adsorbent (Dąbrowski, 2001; Yagub *et al*., 2014).

4.4 Adsorption kinetic studies

4.4.1 Pseudo-first-order kinetic model

Pseudo-first-order kinetic model are generally used to study the dynamic of the dye adsorption process from aqueous solution (Al-Rashed & Al-Gaid, 2012). Figure 4.23, 4.24 and 4.25 shows the plots of $log\ (q_e - q_t)$ versus t for the adsorption of malachite green dye onto raw, acid-alkali treated and microwave-acid-alkali treated *Casuarina equisetifolia* plant seeds, respectively. It can be seen that the R^2 values of all three adsorbents is less than 1, which are from 0.6961 to 0.9045.

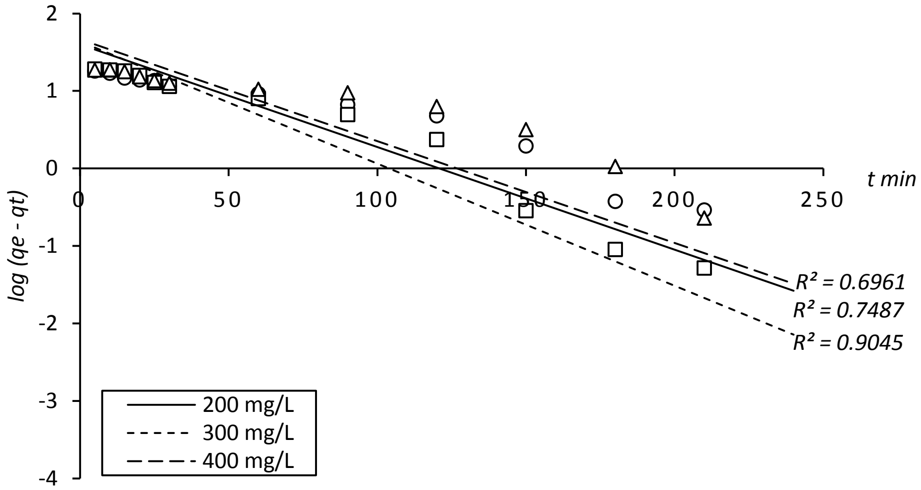


Figure 4.23: Pseudo-first-order reaction of MG adsorption on raw *C. equisetifolia* seeds

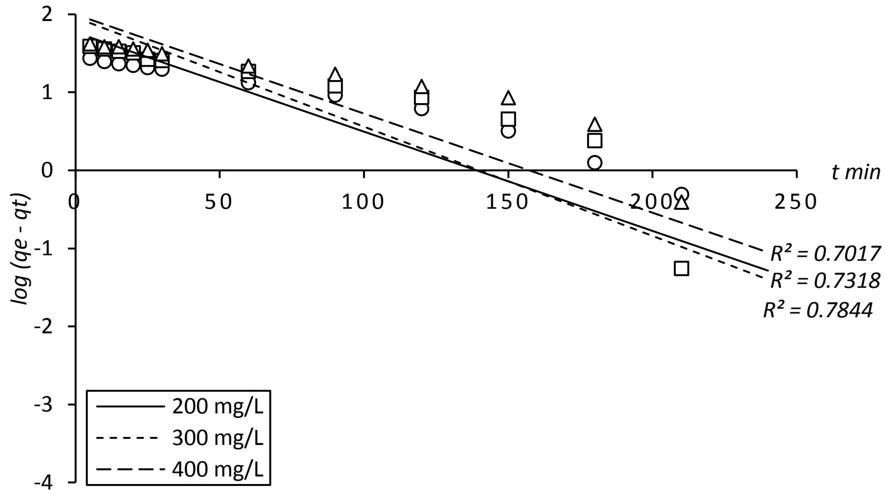


Figure 4.24: Pseudo-first-order reaction of MG adsorption on acid-alkali treated *C. equisetifolia* seeds

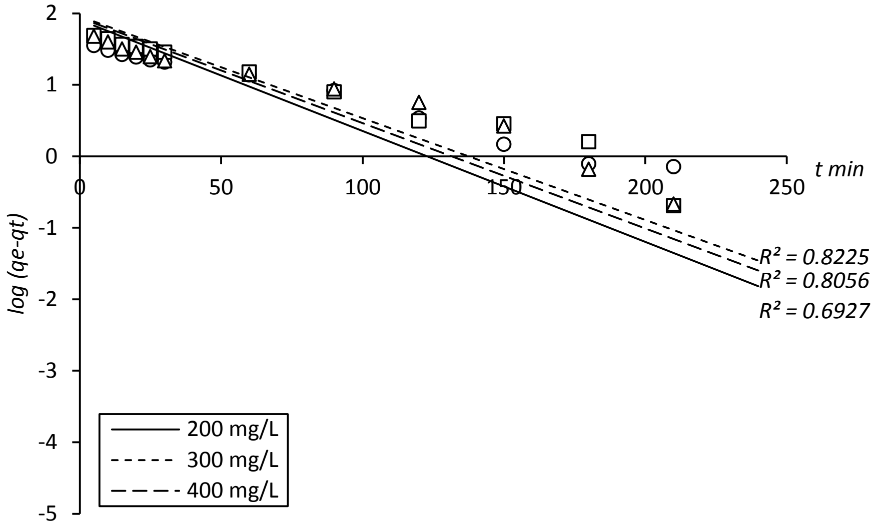


Figure 4.25: Pseudo-first-order reaction of MG adsorption on microwave-acid-alkali treated *C. equisetifolia* seeds

Figure 4.26, 4.27 and 4.28 show pseudo-first-order kinetic model fitting with experimental data for varying NR dye concentration of raw, acid-alkali, and microwave-acid-alkali treated *C. equisetifolia* seeds, respectively. The linear correlation coefficient, R^2 obtained from the plots has low values which are from 0.7272 to 0.8991 at different initial concentration of dye.

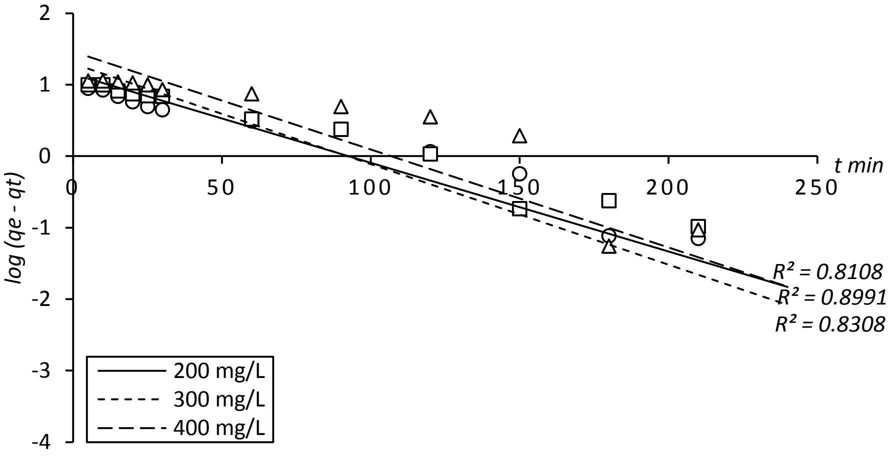


Figure 4.26: Pseudo-first-order reaction of NR adsorption on raw *C. equisetifolia* seeds

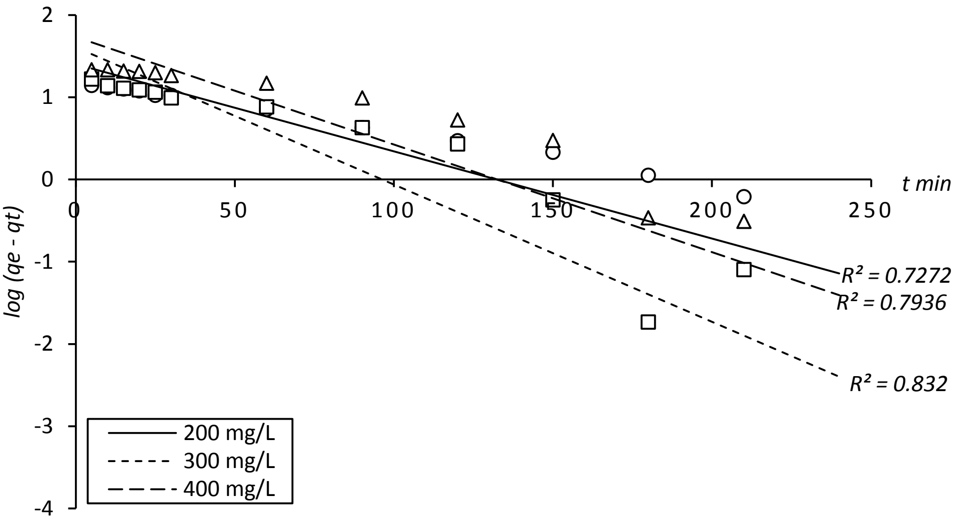


Figure 4.27: Pseudo-first-order reaction of NR adsorption on acid-alkali treated *C. equisetifolia* seeds

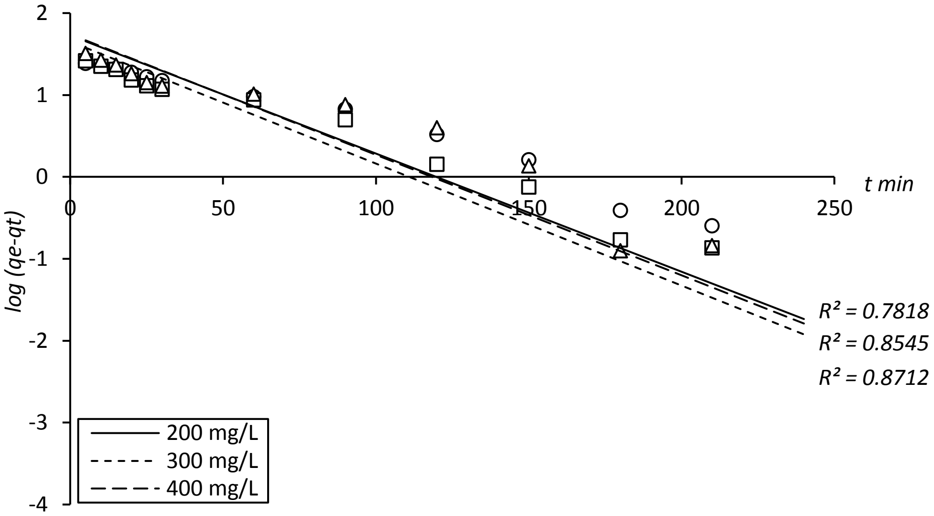


Figure 4.28: Pseudo-first-order reaction of NR adsorption on microwave-acid-alkali treated *C. equisetifolia* seeds.

The parameter of pseudo-first-order models for MG and NR dye are recorded in Table 4.11. All the pseudo-first-order plots of MG and NR dyes adsorption onto adsorbents from *C. equisetifolia* seeds give very poor linear regression coefficient, R^2. The results show that the model does not fitted the experiment data for all three adsorbents. Besides, the model does not reproduce the adsorption kinetic of MG and NR dyes on the adsorbent because the experimental q_e values did not adequate and close to the calculated ones. There are differences in the q_e values because the presence of time lag which is due to the external resistance or boundary layer controlling at the beginning of the adsorption process (Kumar *et al*., 2014).

Table 4.11: Parameters of the pseudo-first-order models for both MG and NR at different concentrations

Malachite green dye					
Adsorbent	**Dye concentration (mg/L)**	**q_e (mg/g) experimental**	**k_1 (min^{-1})**	**q_e (mg/g) calculated**	**R^2**
Raw seeds	200	20.57	0.0304	39.78	0.7487
	300	21.15	0.0364	43.31	0.9045
	400	21.39	0.0302	46.43	0.6961
Acid-alkali treated seeds	200	31.20	0.0292	58.78	0.7318
	300	39.43	0.0322	90.57	0.7844
	400	44.73	0.0292	99.27	0.7017
Microwave-acid-alkali treated seeds	200	42.36	0.0357	80.32	0.6927
	300	52.33	0.0327	90.87	0.8225
	400	51.71	0.0339	86.56	0.8056
Neutral red dye					
Raw seeds	200	10.38	0.0286	14.07	0.8991
	300	11.47	0.0325	19.71	0.8308
	400	11.89	0.0316	29.01	0.8108
Acid-alkali treated seeds	200	17.95	0.0244	25.19	0.7277
	300	20.58	0.0385	40.48	0.8320
	400	21.72	0.0302	53.86	0.7936
Microwave-acid-alkali treated seeds	200	29.53	0.0332	53.70	0.7818
	300	32.43	0.0343	44.84	0.8712
	400	37.41	0.0339	55.25	0.8545

4.4.2 Pseudo-second-order kinetic model

Figure 4.29, 4.30 and 4.31 present the plots of t/q_t versus t for the adsorption of malachite green onto raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds, respectively. The correlation coefficients R^2 values of pseudo-second-order model for adsorption of MG dye are between 0.9384 and 0.9978. For all three adsorbents, the R^2 values are close to 1, which confirms that the MG and NR adsorption follow the pseudo-second-order model.

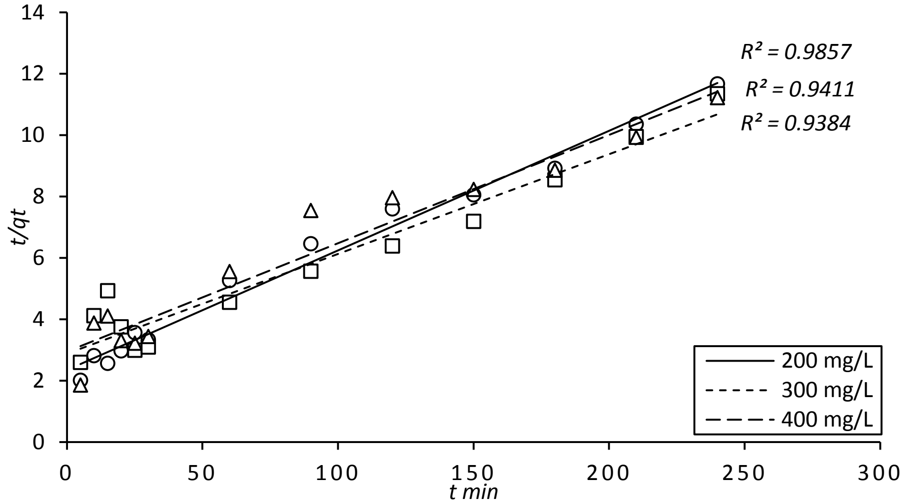


Figure 4.29: Pseudo-second-order reaction of MG adsorption on raw *C. equisetifolia* seeds

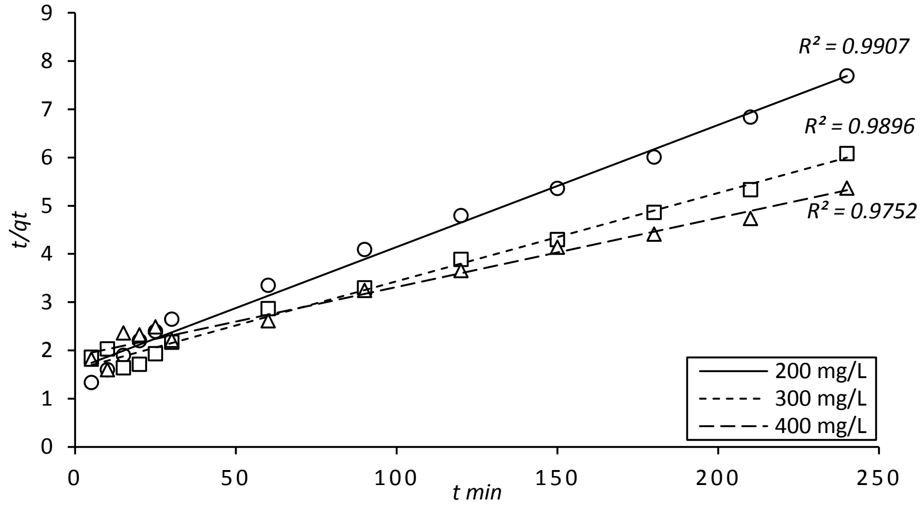


Figure 4.30: Pseudo-second-order reaction of MG adsorption on acid-alkali *C. equisetifolia* seeds

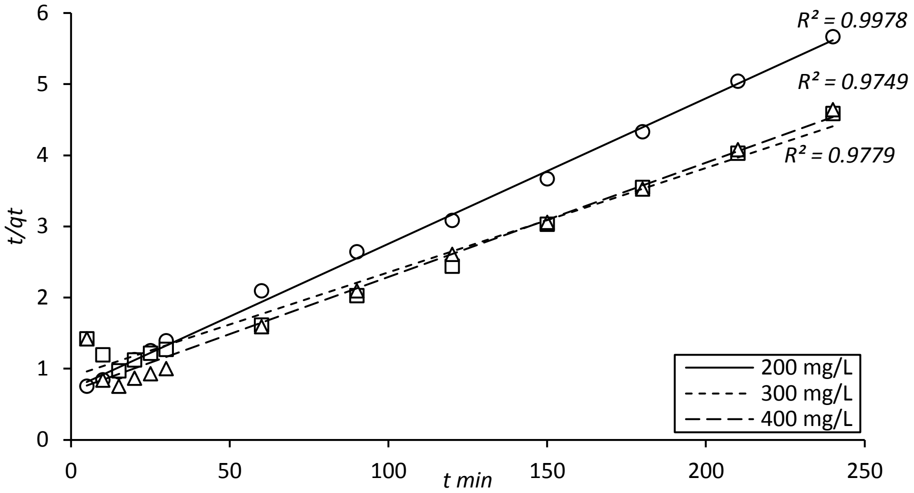


Figure 4.31: Pseudo-second-order reaction of MG adsorption on microwave-acid-alkali *C. equisetifolia* seeds

Figure 4.32, 4.33 and 4.34 show the plots of *t/qt* versus *t* for the adsorption of NR onto raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds, respectively. From the figures, the correlation coefficient, R^2 for model of the adsorption of NR dyes onto *C. equisetifolia* seeds has values close to 1 which are from 0.793 to 0.998. From the R^2 values, it can be concluded that the pseudo-second-order model fitted the experimental data for all three adsorbent from *C. equisetifolia* seeds. Similar observations were reported onto the adsorption of Congo red dye from aqueous solution using cashew nut shell. The study revealed that the adsorption data were well suggested by pseudo-second-order kinetics. The model was based on the assumption that the rate-limiting step of dye onto adsorbent may be chemisorption (Kumar *et al.*, 2010).

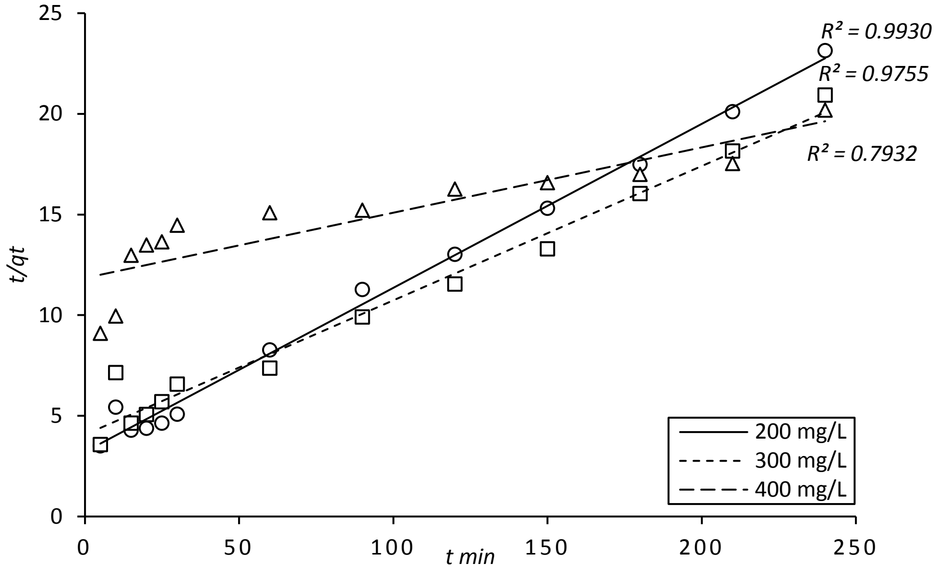


Figure 4.32: Pseudo-second-order reaction of NR adsorption on raw *C. equisetifolia* seeds

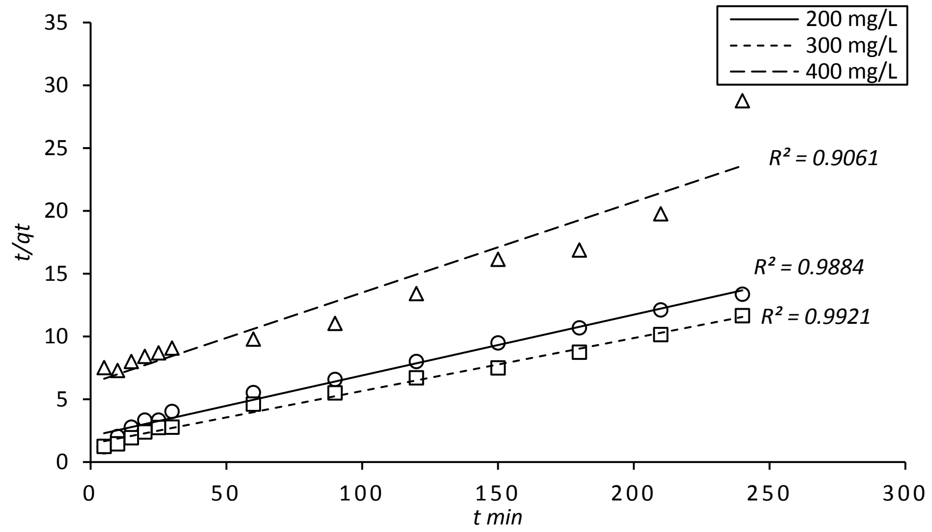


Figure 4.33: Pseudo-second-order reaction of NR adsorption on acid-alkali *C. equisetifolia* seeds

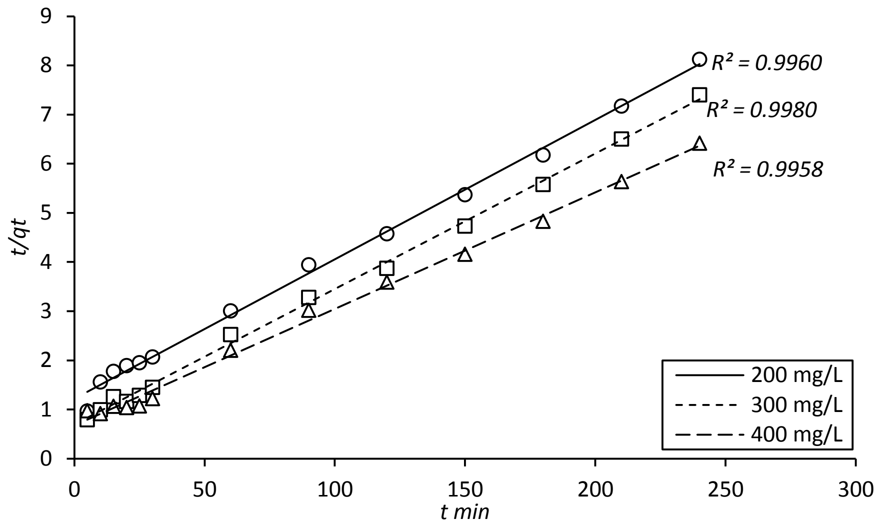


Figure 4.34: Pseudo-second-order reaction of NR adsorption on microwave-acid-alkali *C. equisetifolia* seeds

The pseudo-second-order parameters calculated for raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds for different initial MG and NR dye concentration are showed in Table 4.12. The value of linear correlation coefficients, R^2 for pseudo-second-order are higher compared to pseudo-first-order model and the theoretical q_e values are closer to the experimental q_e values under different initial dye concentration. The pseudo-second-order model is based on assumption of rate-limiting which chemisorption involving valence forces through sharing or exchange of electron between adsorbate and adsorbent was happened (Mohan, Singh, & Singh, 2006). From the results, when the initial dye concentration was increased, the adsorption rate, k_2 was decreased and increased at 400 mg/L. Similar relationship of initial concentration on k_2 values have been reported consistently in many studies (Maldhure & Ekhe, 2011; Pezoti *et al.*, 2014).

Table 4.12: Parameters of the pseudo-second-order models for both MG and NR at different concentrations

Adsorbent	Dye concentration (mg/L)	q_e (mg/g) experimental	k_2 (g/mg.min)	q_e (mg/g) calculated	h (mg/g.min)	R^2
			Malachite green dye			
Raw seeds	200	20.57	0.00064	25.71	0.0000	0.9857
	300	21.15	0.00037	30.77	0.3467	0.9384
	400	21.39	0.00042	28.33	0.3392	0.9411
Acid-alkali treated seeds	200	31.20	0.00040	39.53	0.6195	0.9907
	300	39.43	0.00004	95.24	0.3434	0.9896
	400	44.73	0.00011	69.93	0.5318	0.9752
Microwave-acid-alkali treated seeds	200	42.36	0.00059	48.78	1.4100	0.9978
	300	52.33	0.00024	68.03	1.1271	0.9779
	400	51.71	0.00038	62.11	1.4697	0.9749
			Neutral red dye			
Raw seeds	200	10.38	0.00206	12.29	0.3103	0.9930
	300	11.47	0.00109	14.99	0.2454	0.9755
	400	11.89	0.00009	30.84	0.0000	0.7932
Acid-alkali treated seeds	200	17.95	0.00114	20.66	0.4870	0.9884
	300	20.58	0.00121	23..75	0.6851	0.9921
	400	21.72	0.00083	13.83	0.0000	0.9061
Microwave-acid-alkali treated seeds	200	29.53	0.00066	35.21	0.8224	0.9960
	300	32.43	0.00110	36.23	1.4436	0.9980
	400	37.41	0.00083	42.19	1.4819	0.9958

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this research, three different adsorbents from *C. equisetifolia* seeds were characterized in order to study the properties of the seeds for dye adsorption application. From the results, it was clear that the treatment onto *C. equisetifolia* seeds affected the chemical and morphological properties of the adsorbents. The study of chemical composition showed the lowest percentage for extraneous materials in the microwave-acid-alkali treated *C. equisetifolia* seeds. This indicated that the unwanted materials were successfully extracted during modification by microwave, acid and alkali treatment. The study also revealed the presence of holocellulose, alpha-cellulose, hemicellulose and lignin on the adsorbents from *C. equisetifolia* seeds. The composition were proven to be similar with lignocellulosic waste composition from other studies.

FTIR spectra of the adsorbents form *C. equisetifolia* seeds revealed the presence of various functional group on the adsorbent such as O – H groups, C – H stretch, C=O stretch, C=C bond and C – O bonds which suitable for the adsorption. The spectra of all adsorbents have similar characteristics but slightly changes in peaks and differences in the intensity of the band. Microwave-acid-alkali treated *C. equisetifolia* seeds have higher intensity of C-H stretch at band 2924 cm^{-1} which indicated the presence of cellulose and hemicellulose on the adsorbent. Other bands at 1701-1720 cm^{-1} and 1022-1026 cm^{-1} also showed an increase in intensity which presented the C=O stretch and C-O group, respectively. The involvement of these functional groups were required because they can enhance the adsorption capacity towards dye.

SEM observations of raw, acid-alkali and microwave-acid-alkali treated *C. equisetifolia* seeds indicated that microwave-acid-alkali treated seeds had a relatively rough, coarse and irregular surface structure. SEM micrographs revealed that the surface of the microwave-acid-alkali treated *C. equisetifolia* seeds was full of cavities and cracks compared with raw and acid-alkali treated *C. equisetifolia* seeds. These well-developed surface for adsorbents is a good feature for encouraging adsorption and trapping of dye. Besides, surface charge of the adsorbents showed negative values of zeta potential which is associated to the negatively charge ion of carboxyl and phenolic OH groups that can promote the binding of cationic dyes.

C. equisetifolia seeds has shown a potential to remove MG and NR from aqueous solution. The results of batch adsorption studies presented that the percentage of dye removal were found to agree with the effect of contact time, initial dye concentration and adsorbent dosage. The adsorption of both dyes was sharply increased from 5 to 60 min and reached equilibrium beyond 150 min. The percentage removal of dye was decreased with an increase in initial dye concentration. It showed that the highest percentage was achieved at 200 mg/L for all adsorbents from *C. equisetifolia* seeds.

Meanwhile, the amount of dye adsorbed per unit gram of adsorbent was increased with the increase of initial dye concentration. The highest amount of MG and NR dye adsorbed was at 400 mg.L^{-1} on the microwave-acid-alkali treated *C. equisetifolia* seeds which are 51.33 and 37.41 mg.g^{-1}, respectively.

Furthermore, the percentage removal of dye was increased with the increase in adsorbent dosage from 0.2 to 1.0 g. Microwave-acid-alkali treated *C. equisetifolia* seeds has highest percentage removal of dye. The highest percentage removal of MG and NR dye for microwave-acid-alkali treated seeds was at 1.0 g which are 95.96 and 97.24 %, respectively. The adsorption capacity reduced as the adsorbent dosage increased for both dyes. The maximum adsorption capacity was at 0.2 g of adsorbent and on the microwave-acid-alkali treated seeds which are 78.08 and 42.34 mg.g^{-1}, respectively.

Two types of isotherms, Langmuir and Freundlich model were used to investigate the adsorption of the dye onto *C. equisetifolia* seeds. The isotherm fitted the Langmuir model with high correlation coefficient 0.984 to 0.999. According to Langmuir model, the maximum adsorption capacity for MG and NR dye was obtained with a value of q_{max} of 53.76 and 42.74 mg.g^{-1} for microwave-acid-alkali treated *C. equisetifolia* seeds. The equilibrium parameter, R_L for both dyes was larger than 0 but less than 1 indicating that Langmuir model is favourable.

The interactions of the dye adsorption and *C. equisetifolia* seeds were tested for both pseudo-first-order and pseudo-second-order kinetics. The findings suggested that the adsorption followed pseudo-second-order kinetic model with correlation coefficient between 0.7932 and 0.9980 for both dyes. Besides, the theoritical q_e values are closer to the experimental q_e values under different initial dye concentration. The best fit of correlation coefficient of pseudo-second-order kinetics shows that the rate-limiting step may be chemisorption that involving valence force over exchange or sharing of electron, and the adsorption mechanism depend on the adsorbate and adsorbent.

Therefore, according to the characterization and performance studies that have been conductedin this reseaech, the adsorbents from *C. equisetifolia* seeds were found to be an effective adsorbent and can be as a potential replacement for activated carbon and other adsorbents in the adsorption of cationic dyes, malachite green and neutral red dyes.

5.2 Recommendations

Based on the above conclusions, a few recommendations are drawn for the future research:

i) Characterization of the chemical properties of the adsorbent should be tested using other techniques such as elemental analysis. The elemental analysis of the adsorbent can be evaluated by using energy dispersive spectroscopy (EDS). This techniques was used to determine the element present in the adsorbent such as carbon, oxygen, silicon, nitrogen, hydrogen and sulphur.

ii) The crystal texture and crystalline of the adsorbent can be defined by using X-ray diffraction (XRD). The determination of crystalline of the adsorbent are also important in order to study the surface structure of adsorbent which can enhance the removal of pollutants.

iii) The study on the pore size distribution (PSD) should be considered in the characterization of microporous adsorbent. Various techniques can be used to determine the PSD of adsorbent such as density functional theory (DFT) or potential-theory method like Horvath-Kawazoe (HK) equation. The determination of PSD allows the study on the division of the total pore volume available to molecules of a given size and shape.

iv) Further study on desorption of the adsorbent should be tested in order to recover sequestered dye ions and regenerate the adsorbents. Desorption studies show the irreversible nature of the sorption reaction between the adsorbents and dye molecules. Desorption experiment can be studied by agitating the loaded adsorbent with distilled water, and then the suspension is filtered and the liquid phase will be analysed.

v) Other parameter such as the effect of pH of dye solution, particle size of the adsorbent and ionic strength should be considered in the batch adsorption experiments in order to study the potential of *C. equisetifolia seeds* as adsorbent.

vi) As well as Langmuir and Freundlich isotherm model, other isotherm models can be used to describe the isotherm curve such as Temkin, Toth and Dubinin-Radushkevich (D-R) isotherm models. Various type of isotherm models can be used in this research in order to create the most fitting correlation for the equilibrium data of an adsorption system in the removal of adsorbate.

vii) The use of other adsorbates such as industrial wastewater, metal ions and other dyes should be considered for future study in order to investigate the effectiveness of *C. equisetifolia seeds* in the removal of various pollutants. Besides, the usefulness of adsorbents can be considered in the removal of dye-based wastewater from industrial effluents.

viii) A sequences of column test should be accomplished to study the breakthrough characteristics, by varying the functioning parameters, adsorbent bed height and hydraulic loading rate. Column test are accomplished to evaluate the efficacy of adsorbent in removing contaminants from wastewater and it has been successfully applies in contaminant removal such as in removal of arsenic using adsorbent media.

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APPENDIX A

CHARACTERIZATION OF ADSORBENT

i. Chemical composition of *Casuarina equisetifolia* seeds

Table A.1: Test performed of chemical composition of *Casuarina equisetifolia* seeds

Test	**Methodology**
Moisture content	TAPPI T264 cm-97, Preparation of Wood for Chemical Analysis
Ethanol-toluene solubility	TAPPI T204 cm-97, Solvent Extraxtives of Wood and Pulp
Holocellulose content	Wise, L.E., Murphy, M. & D'Addieco, A.A. 1946. Chlorite holocelullose: Its fractionation and bearing on summative wood analysis and on studies on the hemicellulose, *Paper Trade Journal* **122** (2):35-43
Alpha-cellulose content	TAPPI T203 om-93 Alpha-, Beta-, and Gamma-Cellulose in Pulp
Lignin content	TAPPI T222 om-02 Acid-Insoluble Lignin in Wood and Pulp
Ash	TAPPI T211 om-02. Ash in Wood, Pulp, Paper and Paperboard: Combustion at 525°C
Hot water solubility	TAPPI T207 cm-99. Water Solubility of Wood and Pulp
NaOH solubility	TAPPI T212 om-02. One Percent Sodium Hydroxide Solubility of Wood and Pulp
Pentosan	Savard, J., Besson, A., & Morize, S. 1954. Analysis Chimique des Bois Tropicaux. Tome II. Publ. Centre Tech. For. No. 16. Paris:t:pt.

Table A.2: Chemical composition of raw *Casuarina equisetifolia* seeds

Description	Average (%)	Standard deviation (%)	No. of replicates
Moisture content	9.6	0.1	3
Ethanol-toluene solubility	3.0	0.3	3
Holocellulose content	60.7	1.7	2
Alpha-cellulose content	24.1	1.2	2
Lignin content	45.2	1.0	3
Ash	2.2	0.02	3
Hot water solubility	9.2	0.2	3
NaOH solubility	30.0	1.1	3
Pentosan	17.0	0.1	3

Table A.3: Chemical composition of acid-alkali treated *Casuarina equisetifolia* seeds

Description	Average (%)	Standard deviation (%)	No. of replicates
Moisture content	10.5	0.0	3
Ethanol-toluene solubility	2.7	0.3	3
Holocellulose content	57.0	1.4	2
Alpha-cellulose content	25.8	1.2	2
Lignin content	50.0	1.0	3
Ash	1.9	0.02	3
Hot water solubility	5.5	0.2	3
NaOH solubility	28.4	1.1	3
Pentosan	10.8	0.1	3

Table A.4: Chemical composition of microwave-acid-alkali treated *Casuarina equisetifolia* seeds

Description	Average (%)	Standard deviation (%)	No. of replicates
Moisture content	9.4	0.6	3
Ethanol-toluene solubility	2.4	0.1	3
Holocellulose content	56.0	1.1	2
Alpha-cellulose content	25.2	0.9	2
Lignin content	50.2	0.3	3
Ash	2.1	0.1	3
Hot water solubility	4.5	0.2	3
NaOH solubility	27.5	0.4	3
Pentosan	14.3	0.1	3

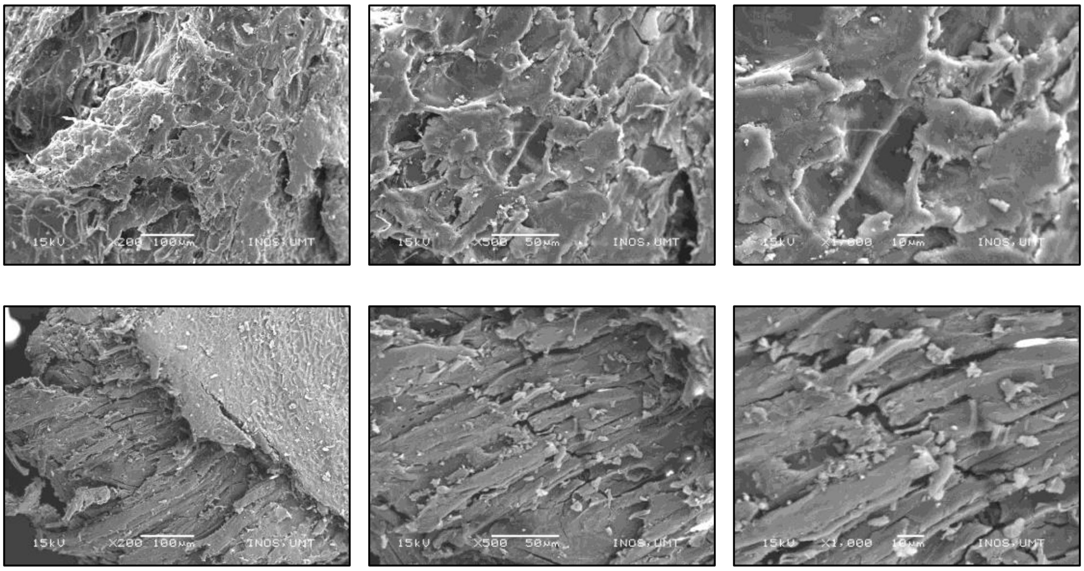
* Example calculation of hemicellulose content

Hemicellulose content (%) = Holocelullulose content – alpha-cellulose content

= 56.0 – 25.2

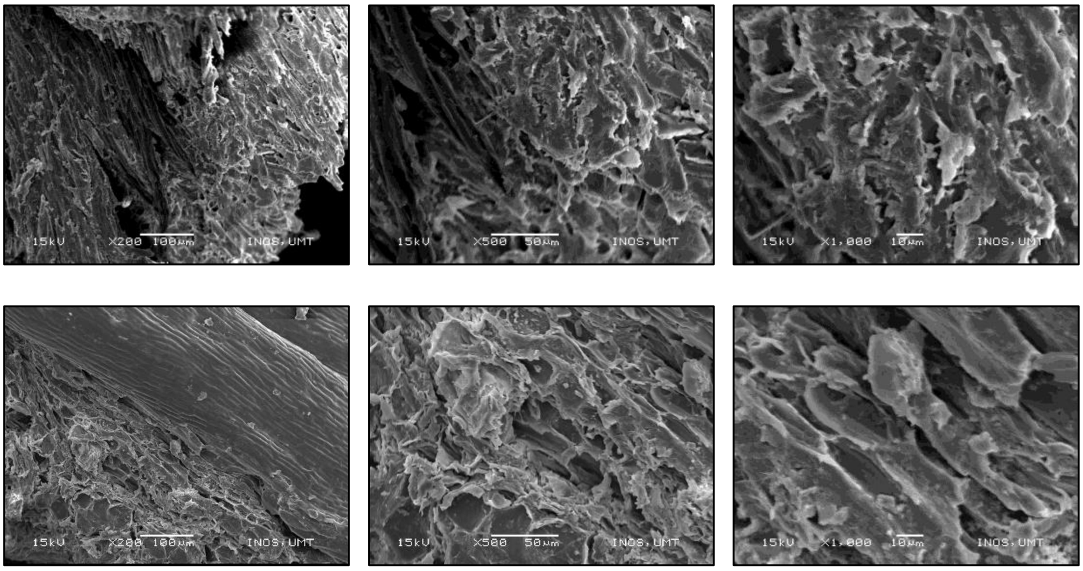
= 30.8 %

ii. Surface morphology of *C. equisetifolia* seeds



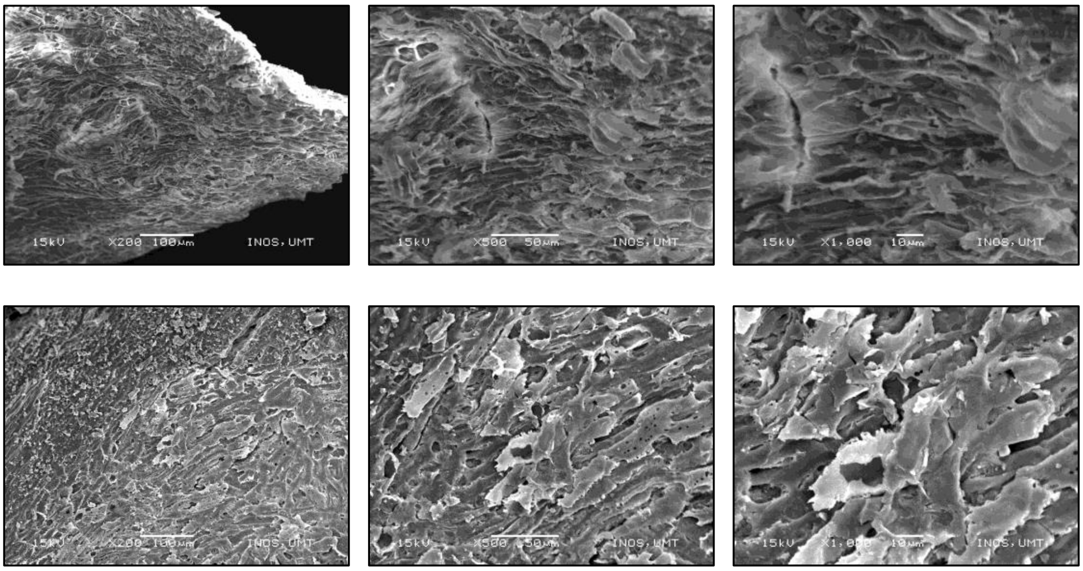
200 x 500 x 1000 x

Figure A.1: Surface morphology of raw *C. equisetifolia* seeds



200 x 500 x 1000 x

Figure A.2: Surface morphology of acid-alkali treated *C. equisetifolia* seeds



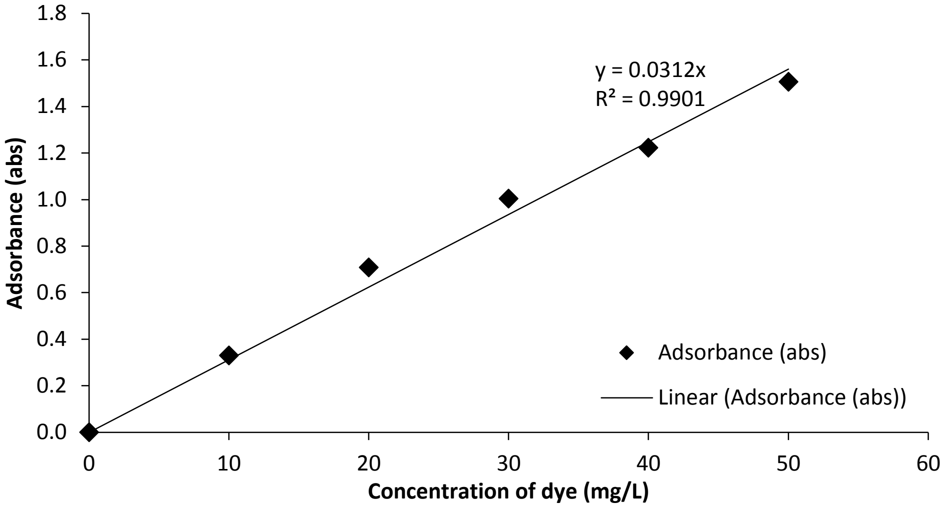
200 x 500 x 1000 x

Figure A.2: Surface morphology of microwave-acid-alkali treated *C. equisetifolia* seeds

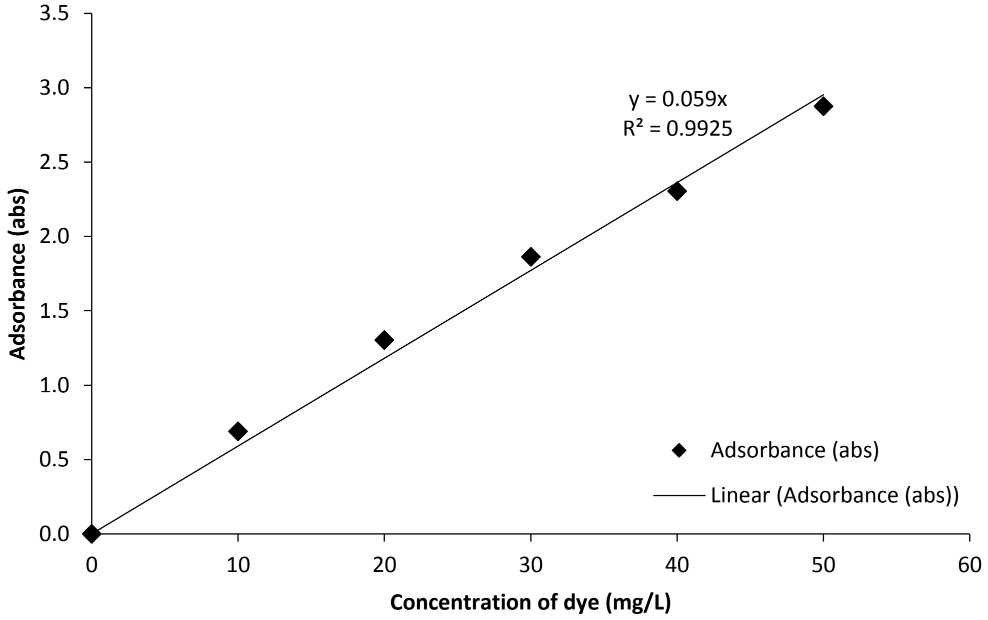
APPENDIX B

STANDARD CURVE OF DYES

i. Standard curve of malachite green dye



ii. Standard curve of neutral red dye



APPENDIX C

BATCH ADSORPTION STUDY

i. Raw *Casuarina equisetifolia* seeds

a) Effect of different initial malachite green dye concentration

C.1: Absorbance readings for malachite green dye

Time (min)	Absorbance of dye (abs)		
	200 mg/L	300 mg/L	400 mg/L
0	1.563	0.961	0.635
5	1.486	0.937	0.619
10	1.452	0.931	0.619
15	1.381	0.923	0.613
20	1.353	0.895	0.598
25	1.345	0.857	0.587
30	1.282	0.840	0.581
60	1.208	0.797	0.568
90	1.129	0.760	0.561
120	1.070	0.727	0.541
150	0.982	0.701	0.522
180	0.933	0.699	0.509
210	0.931	0.698	0.503
240	0.922	0.697	0.502

C.2: Concentration of malachite green dye

Time (min)	Concentration of dye (mg/L)		
	200 mg/L	300 mg/L	400 mg/L
0	200.43	308.12	407.34
5	190.47	300.42	396.58
10	186.20	298.40	397.01
15	177.05	295.94	392.74
20	173.50	286.79	383.12
25	172.39	274.72	376.28
30	164.40	269.38	372.44
60	154.83	255.43	364.10
90	144.70	243.46	359.62
120	137.22	232.99	347.05
150	125.96	224.66	334.49
180	119.66	223.88	326.06
210	119.32	223.73	322.72
240	118.15	223.52	321.80

b) Effect of different initial neutral red dye concentration

C.3: Absorbance readings for neutral red dye

Time (min)	Absorbance of dye (abs)		
	200 mg/L	300 mg/L	400 mg/L
0	2.979	1.803	1.180
5	2.895	1.770	1.174
10	2.870	1.770	1.173
15	2.773	1.726	1.169
20	2.710	1.710	1.166
25	2.661	1.699	1.158
30	2.631	1.695	1.141
60	2.551	1.611	1.128
90	2.508	1.589	1.098
120	2.436	1.558	1.082
150	2.401	1.536	1.063
180	2.371	1.538	1.041
210	2.363	1.530	1.039
240	2.367	1.532	1.040

C.4: Concentration of neutral red dye

Time (min)	Concentration of dye (mg/L)		
	200 mg/L	300 mg/L	400 mg/L
0	201.97	305.54	400.07
5	196.27	299.94	398.07
10	194.60	299.94	397.66
15	187.98	292.60	396.38
20	183.71	289.77	395.37
25	180.41	287.99	392.66
30	178.40	287.29	386.89
60	172.95	272.99	382.49
90	170.03	269.24	372.32
120	165.12	263.99	366.89
150	162.76	260.42	360.29
180	160.77	260.64	352.76
210	160.18	259.26	352.16
240	160.47	259.68	352.53

c) Effect of different adsorbent dosage for malachite green dye removal

C.5: Absorbance readings for malachite green dye

Time (min)	Absorbance of dye (abs)				
	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g
0	1.566	1.563	1.567	1.560	1.574
5	1.462	1.486	1.378	1.358	1.282
10	1.446	1.452	1.374	1.264	1.177
15	1.410	1.381	1.297	1.216	1.096
20	1.415	1.353	1.293	1.148	1.006
25	1.414	1.345	1.262	1.084	0.972
30	1.411	1.282	1.227	1.014	0.908
60	1.368	1.208	1.088	0.877	0.736
90	1.317	1.129	0.942	0.759	0.590
120	1.301	1.070	0.814	0.633	0.494
150	1.265	0.982	0.772	0.580	0.428
180	1.229	0.933	0.751	0.576	0.394
210	1.214	0.931	0.734	0.539	0.344
240	1.197	0.922	0.741	0.509	0.335

C.6: Concentration of malachite green dye

Time (min)	Concentration of dye (mg/L)				
	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g
0	200.73	200.43	200.94	200.03	201.76
5	187.44	190.47	176.67	174.06	164.40
10	185.34	186.20	176.20	162.01	150.90
15	180.77	177.05	166.24	155.90	140.51
20	181.45	173.50	165.77	147.22	128.93
25	181.28	172.39	161.84	139.02	124.57
30	180.94	164.40	157.31	129.96	116.37
60	175.43	154.83	139.49	112.39	94.40
90	168.80	144.70	120.83	97.26	75.64
120	166.84	137.22	104.36	81.20	63.29
150	162.22	125.96	98.98	74.40	54.91
180	157.56	119.66	96.32	73.80	50.51
210	155.60	119.32	94.10	69.10	44.15
240	153.50	118.15	94.96	65.21	42.99

d) Effect of different adsorbent dosage for neutral red dye removal

C.7: Absorbance readings for neutral red dye

Time (min)	Absorbance of dye (abs)				
	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g
0	2.974	2.979	2.948	2.952	2.937
5	2.929	2.895	2.815	2.695	2.776
10	2.888	2.870	2.728	2.632	2.522
15	2.870	2.773	2.724	2.626	2.453
20	2.846	2.710	2.712	2.608	2.285
25	2.805	2.661	2.642	2.467	2.208
30	2.766	2.631	2.518	2.429	2.072
60	2.730	2.551	2.289	2.192	1.770
90	2.726	2.508	2.209	2.069	1.574
120	2.684	2.436	2.184	2.012	1.488
150	2.658	2.401	2.138	1.950	1.394
180	2.584	2.371	2.044	1.859	1.336
210	2.552	2.363	2.038	1.828	1.280
240	2.544	2.367	2.052	1.827	1.274

C.8: Concentration of neutral red dye

Time (min)	Concentration of dye (mg/L)				
	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g
0	201.63	201.97	199.84	200.16	199.10
5	198.60	196.27	190.87	182.69	188.20
10	195.77	194.60	184.97	178.46	171.01
15	194.58	187.98	184.66	178.03	166.31
20	192.95	183.71	183.86	176.80	154.94
25	190.15	180.41	179.11	167.28	149.69
30	187.55	178.40	170.71	164.70	140.47
60	185.11	172.95	155.21	148.58	119.98
90	184.84	170.03	149.74	140.27	106.70
120	181.99	165.12	148.05	136.43	100.86
150	180.20	162.76	144.97	132.18	94.49
180	175.19	160.77	138.58	126.06	90.60
210	173.02	160.18	138.17	123.95	86.80
240	172.47	160.47	139.14	123.84	86.37

ii. Acid-alkali treated *Casuarina equisetifolia* seeds

a) Effect of different initial malachite green dye concentration

C.9: Absorbance readings for malachite green dye

Time (min)	Absorbance of dye (abs)		
	200 mg/L	300 mg/L	400 mg/L
0	1.571	0.946	0.633
5	1.454	0.937	0.616
10	1.376	0.905	0.594
15	1.325	0.876	0.593
20	1.288	0.855	0.579
25	1.245	0.785	0.570
30	1.217	0.774	0.548
60	1.012	0.686	0.490
90	0.885	0.606	0.460
120	0.791	0.562	0.428
150	0.697	0.511	0.407
180	0.636	0.484	0.378
210	0.613	0.455	0.356
240	0.597	0.454	0.354

C.10: Concentration of malachite green dye

Time (min)	Concentration of dye (mg/L)		
	200 mg/L	300 mg/L	400 mg/L
0	201.37	303.35	405.56
5	186.37	300.44	394.57
10	176.41	290.17	380.60
15	169.83	280.64	380.15
20	165.09	273.91	371.15
25	159.62	251.65	365.43
30	156.03	248.12	351.26
60	129.74	219.76	313.80
90	113.46	194.23	294.76
120	101.37	180.04	274.36
150	89.41	163.87	260.74
180	81.58	155.26	242.31
210	78.55	145.86	228.21
240	76.58	145.63	226.64

b) Effect of different initial neutral red dye concentration

C.11: Absorbance readings for neutral red dye

Time (min)	Absorbance of dye (abs)		
	200 mg/L	300 mg/L	400 mg/L
0	2.948	1.813	1.180
5	2.710	1.719	1.178
10	2.661	1.652	1.179
15	2.631	1.630	1.169
20	2.595	1.616	1.166
25	2.508	1.600	1.158
30	2.509	1.560	1.141
60	2.308	1.507	1.099
90	2.141	1.428	1.039
120	2.064	1.391	0.986
150	2.015	1.341	0.959
180	1.955	1.328	0.928
210	1.925	1.326	0.928
240	1.889	1.327	0.924

C.12: Concentration of neutral red dye

Time (min)	Concentration of dye (mg/L)		
	200 mg/L	300 mg/L	400 mg/L
0	199.86	307.29	400.10
5	183.71	291.30	399.41
10	180.41	279.94	399.66
15	178.40	276.33	396.38
20	175.95	273.95	395.37
25	170.03	271.13	392.66
30	170.12	264.35	386.89
60	156.47	255.42	372.49
90	145.15	242.03	352.32
120	139.91	235.82	334.29
150	136.60	227.24	325.14
180	132.54	225.06	314.60
210	130.52	224.67	314.47
240	128.05	224.99	313.23

c) Effect of different adsorbent dosage for malachite green dye removal

C.13: Absorbance readings for malachite green dye

Time (min)	Absorbance of dye (abs)				
	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g
0	1.561	1.571	1.569	1.561	1.567
5	1.549	1.454	1.525	1.525	1.220
10	1.523	1.376	1.300	1.027	0.860
15	1.517	1.325	1.050	0.856	0.697
20	1.509	1.288	0.954	0.746	0.547
25	1.482	1.245	0.903	0.699	0.466
30	1.477	1.217	0.893	0.659	0.399
60	1.310	1.012	0.759	0.512	0.283
90	1.163	0.885	0.683	0.416	0.219
120	1.032	0.791	0.629	0.358	0.180
150	0.955	0.697	0.569	0.320	0.145
180	0.873	0.636	0.531	0.269	0.124
210	0.864	0.613	0.502	0.259	0.121
240	0.858	0.597	0.486	0.247	0.117

C.14: Concentration of malachite green dye

Time (min)	Concentration of dye (mg/L)				
	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g
0	200.13	201.37	201.13	200.13	200.90
5	198.60	186.37	195.56	195.56	156.37
10	195.26	176.41	166.71	131.67	110.21
15	194.49	169.83	134.57	109.70	89.32
20	193.46	165.09	122.35	95.60	70.18
25	190.03	159.62	115.81	89.62	59.79
30	189.33	156.03	114.53	84.48	51.15
60	167.99	129.74	97.31	65.62	36.24
90	149.10	113.46	87.56	53.31	28.04
120	132.35	101.37	80.64	45.84	23.07
150	122.39	89.41	72.91	40.97	18.57
180	111.93	81.58	68.03	34.53	15.85
210	110.78	78.55	64.36	33.16	15.55
240	109.97	76.58	62.35	31.67	14.99

d) Effect of different adsorbent dosage for neutral red dye removal

C.15: Absorbance readings for neutral red dye

Time (min)	Absorbance of dye (abs)				
	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g
0	2.971	2.948	2.948	2.973	2.947
5	2.866	2.710	2.712	2.745	2.558
10	2.760	2.661	2.714	2.683	2.474
15	2.717	2.631	2.585	2.676	2.412
20	2.643	2.595	2.528	2.511	2.289
25	2.596	2.508	2.507	2.480	2.187
30	2.559	2.509	2.433	2.370	2.152
60	2.425	2.308	2.146	2.019	1.700
90	2.347	2.141	1.992	1.823	1.329
120	2.290	2.064	1.893	1.635	1.039
150	2.281	2.015	1.848	1.482	0.863
180	2.231	1.955	1.834	1.414	0.749
210	2.201	1.925	1.791	1.410	0.701
240	2.208	1.889	1.761	1.390	0.701

C.16: Concentration of neutral red dye

Time (min)	Concentration of dye (mg/L)				
	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g
0	201.42	199.86	199.84	201.57	199.81
5	194.33	183.71	183.86	186.10	173.40
10	187.11	180.41	184.00	181.88	167.75
15	184.20	178.40	175.25	181.45	163.55
20	179.19	175.95	171.39	170.21	155.19
25	176.02	170.03	169.99	168.11	148.25
30	173.49	170.12	164.94	160.69	145.90
60	164.41	156.47	145.49	136.85	115.23
90	159.14	145.15	135.02	123.59	90.08
120	155.25	139.91	128.33	110.84	70.43
150	154.67	136.60	125.25	100.47	58.51
180	151.23	132.54	124.34	95.84	50.76
210	149.22	130.52	121.40	95.59	47.53
240	149.67	128.05	119.36	94.22	47.50

iii. Microwave treated *Casuarina equisetifolia* seeds

a) Effect of different initial malachite green dye concentration

C.17: Absorbance readings for malachite green dye

Time (min)	Absorbance of dye (abs)		
	200 mg/L	300 mg/L	400 mg/L
0	1.557	0.966	0.627
5	1.349	0.922	0.605
10	1.188	0.862	0.553
15	1.066	0.773	0.503
20	1.004	0.743	0.483
25	0.934	0.710	0.460
30	0.884	0.671	0.440
60	0.663	0.502	0.392
90	0.494	0.412	0.359
120	0.342	0.352	0.340
150	0.281	0.348	0.321
180	0.260	0.333	0.309
210	0.257	0.315	0.306
240	0.235	0.313	0.305

C.18: Concentration of malachite green dye

Time (min)	Concentration of dye (mg/L)		
	200 mg/L	300 mg/L	400 mg/L
0	199.58	309.62	402.14
5	172.98	295.51	388.03
10	152.26	276.18	354.36
15	136.71	247.76	322.39
20	128.72	238.25	309.85
25	119.79	227.46	294.62
30	113.33	215.06	282.26
60	85.04	160.88	251.32
90	63.33	132.20	230.41
120	43.90	112.82	217.95
150	36.03	111.66	205.90
180	33.29	106.71	197.95
210	32.99	101.11	196.15
240	30.13	100.30	195.30

b) Effect of different initial neutral red dye concentration

C.19: Absorbance readings for neutral red dye

Time (min)	Absorbance of dye (abs)		
	200 mg/L	300 mg/L	400 mg/L
0	2.981	1.815	1.206
5	2.677	1.667	1.146
10	2.603	1.577	1.078
15	2.482	1.534	1.040
20	2.358	1.410	0.980
25	2.225	1.356	0.931
30	2.124	1.327	0.917
60	1.804	1.254	0.885
90	1.634	1.167	0.855
120	1.433	1.083	0.812
150	1.334	1.067	0.781
180	1.262	1.054	0.766
210	1.254	1.053	0.766
240	1.239	1.050	0.765

C.20: Concentration of neutral red dye

Time (min)	Concentration of dye (mg/L)		
	200 mg/L	300 mg/L	400 mg/L
0	202.10	307.63	408.81
5	181.49	282.49	388.36
10	176.47	267.34	365.31
15	168.29	259.94	352.54
20	159.89	239.04	332.09
25	150.82	229.89	315.71
30	144.01	224.97	310.73
60	122.28	212.60	300.01
90	110.76	197.85	289.72
120	97.16	183.62	275.14
150	90.43	180.90	264.63
180	85.54	178.59	259.67
210	84.99	178.45	259.75
240	83.98	177.91	259.17

c) Effect of different adsorbent dosage for malachite green dye removal

C.21: Absorbance readings for malachite green dye

Time (min)	Absorbance of dye (abs)				
	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g
0	1.560	1.557	1.562	1.558	1.560
5	1.346	1.349	1.335	1.318	1.240
10	1.177	1.188	1.080	0.930	0.862
15	1.100	1.066	0.883	0.820	0.738
20	1.062	1.004	0.773	0.689	0.597
25	1.012	0.934	0.688	0.609	0.529
30	0.959	0.884	0.668	0.534	0.448
60	0.760	0.663	0.471	0.302	0.227
90	0.599	0.494	0.318	0.203	0.154
120	0.509	0.342	0.215	0.140	0.110
150	0.425	0.281	0.207	0.129	0.099
180	0.362	0.260	0.203	0.111	0.086
210	0.351	0.257	0.193	0.107	0.072
240	0.342	0.235	0.184	0.104	0.063

C.22: Concentration of malachite green dye

Time (min)	Concentration of dye (mg/L)				
	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g
0	200.00	199.58	200.30	199.76	200.00
5	172.56	172.98	171.11	169.02	159.02
10	150.89	152.26	138.42	119.27	110.56
15	141.01	136.71	113.16	105.09	94.65
20	136.20	128.72	99.16	88.38	76.54
25	129.69	119.79	88.26	78.03	67.86
30	122.99	113.33	85.60	68.42	57.44
60	97.44	85.04	60.42	38.72	29.10
90	76.75	63.33	40.80	26.07	19.77
120	65.30	43.90	27.55	17.91	14.11
150	54.53	36.03	26.58	16.58	12.68
180	46.42	33.29	26.03	14.23	10.98
210	45.00	32.99	24.74	13.68	9.19
240	43.85	30.13	23.59	13.38	8.08

d) Effect of different adsorbent dosage for neutral red dye removal

C.23: Absorbance readings for neutral red dye

Time (min)	Absorbance of dye (abs)				
	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g
0	2.952	2.981	2.954	2.975	2.981
5	2.806	2.677	2.581	2.671	2.594
10	2.795	2.603	2.329	2.490	2.001
15	2.686	2.482	2.264	2.095	1.686
20	2.602	2.358	2.099	1.939	1.492
25	2.561	2.225	1.957	1.796	1.347
30	2.414	2.124	1.825	1.645	1.232
60	2.187	1.804	1.453	1.236	0.753
90	2.062	1.634	1.158	0.912	0.491
120	1.883	1.433	0.959	0.697	0.248
150	1.778	1.334	0.796	0.572	0.167
180	1.700	1.262	0.724	0.541	0.123
210	1.707	1.254	0.721	0.525	0.112
240	1.703	1.239	0.737	0.527	0.082

C.24: Concentration of neutral red dye

Time (min)	Concentration of dye (mg/L)				
	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g
0	200.11	202.10	200.30	201.69	202.08
5	190.25	181.49	175.01	181.06	175.84
10	189.52	176.47	157.88	168.84	135.64
15	182.12	168.29	153.51	142.03	114.28
20	176.38	159.89	142.33	131.44	101.13
25	173.62	150.82	132.67	121.79	91.30
30	163.66	144.01	123.69	111.55	83.54
60	148.24	122.28	98.48	83.81	51.03
90	139.81	110.76	78.53	61.83	33.25
120	127.63	97.16	65.04	47.23	16.84
150	120.53	90.43	53.96	38.80	11.34
180	115.25	85.54	49.08	36.70	8.34
210	115.71	84.99	48.88	35.62	7.62
240	115.44	83.98	49.94	35.73	5.58

CALCULATION

i. Final concentration of dye

$$\text{Final concentration of dye, } C_i = \frac{\text{Abs}}{\text{M}} \times \text{DF}$$

where,

Abs is absorbance readings of dye, abs

M is slope of dye standard curve

- Malachite green = 0.0312
- Neutral red = 0.059

DF is dilution factor of dye

- 200 mg/L = 4x
- 300 mg/L = 10x
- 400 mg/L = 20x

*Example of calculation:

Final concentration of neutral red dye at 240 min onto microwave-acid-alkali treated *Casuarina equsetifolia* seeds,

$$\text{Final concentration of dye, } C_i = \frac{0.082}{0.059} \times 4$$

$$= 5.58 \text{ mg/L}$$

ii. Adsorption capacity

$$q_e = \frac{[(C_0 - C_e)\text{V}]}{\text{m}}$$

where,

q_e is adsorption capacity, mg/g

C_0 is initial dye concentration, mg/L

C_e is equilibrium dye concentration, mg/L

V is volume of dye solution, L

m is mass of *Casuarina equisetifolia* plant seeds, g

*Example of calculation:

Adsorption capacity or amount of malachite green dye adsorbed per gram of adsorbent at 200 mg/L dye concentration and 0.4 g of adsorbent dosage,

$$\text{Amount of dye adsorbed, } q_e = \frac{[(200.00 - 31.13 \text{ mg/L})\ 0.1\text{L}]}{0.4 \text{ g}}$$

$$= 42.21 \text{ mg/g}$$

iii. Percentage of dye removal

$$\% \text{ Dye removal} = \frac{(C_0 - C_e)}{C_0} \times 100$$

where,

C_0 is initial dye concentration, mg/L

C_e is equilibrium dye concentration, mg/L

*Example of calculation:

Percentage of 200 mg/L neutral red dye removal at 240 min onto 1.0 g of microwave-acid-alkali treated *Casuarina equisetifolia* seeds,

$$\% \text{ Dye removal} = \frac{(202.08 - 5.58) \text{ mg/L}}{202.08 \text{ mg/L}} \times 100$$

$$= 97.24 \%$$

APPENDIX D

ADSORPTION ISOTHERM

A. Langmuir isotherm

Table D.1: C_e and C_e/q_e for raw *Casuarina equisetifolia* seeds

Malachite green		Neutral red	
C_e	C_e/q_e	C_e	C_e/q_e
118.15	5.743	160.47	15.466
213.52	10.568	259.68	22.650
321.8	15.048	352.53	29.661

Table D.2: C_e and C_e/q_e acid-alkali treated *Casuarina equisetifolia* seeds

Malachite green		Neutral red	
C_e	C_e/q_e	C_e	C_e/q_e
76.58	2.455	128.05	7.133
145.63	3.693	224.99	10.935
226.64	5.067	313.23	14.423

Table D.3: C_e and C_e/q_e for microwave-acid-alkali treated *Casuarina equisetifolia* seeds

*Malachite green		Neutral red	
C_e	C_e/q_e	C_e	C_e/q_e
30.13	0.711	83.98	2.844
100.29	1.917	177.91	5.486
195.30	3.777	259.17	6.923

where, C_e is concentration of dye at equilibrium, (mg/L) and q_e is adsorption capacity or amount of dye adsorbed (mg/g)

*Example of calculation of Langmuir parameter:

For the adsorption of malachite green onto microwave-acid-alkali treated *Casuarina equisetifolia* seeds

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad \text{(Langmuir equation)}$$

y = 0.0186x + 0.1134 (Linear equation of Langmuir plot)

i) q_{max}, maximum adsorption capacity (mg/g)

$$\frac{C_e}{q_{max}} = 0.0186x \qquad \text{where, } C_e = x$$

$$q_{max} = \frac{1}{0.0186}$$

$$= 53.7634 \text{ mg/g}$$

ii) K_L, Langmuir constant (L/mg)

$$\frac{1}{q_{max}K_L} = 0.1134 \qquad \text{where, } q_{max} = 53.7634 \text{ mg/g}$$

$$K_L = \frac{1}{0.1134 \times 53.7634}$$

$$= 0.1640$$

iii) R_L, separation factor

$$R_L = \frac{1}{1 + K_L C_0} \qquad \text{where, } C_0 = \text{maximum initial concentration (mg/L)}$$

$$= \frac{1}{1 + 0.1640 \text{ L/mg} \times 400 \text{ mg/L}}$$

$$= 0.0150$$

B. Freundlich isotherm

Table D.4: *log* C_e and *log* q_e for Raw *Casuarina equisetifolia* seeds

Malachite green		Neutral red	
log C_e	*log* q_e	*log* C_e	*log* q_e
2.072	1.313	2.205	1.016
2.349	1.325	2.414	1.059
2.508	1.330	2.547	1.075

Table D.5: *log* C_e and *log* q_e for acid-alkali treated *Casuarina equisetifolia* seeds

Malachite green		Neutral red	
log C_e	*log* q_e	*log* C_e	*log* q_e
1.884	1.494	2.107	1.254
2.163	1.596	2.352	1.313
2.355	1.651	2.496	1.337

Table D.6: *log* C_e and *log* q_e for Microwave-acid-alkali treated *Casuarina equisetifolia* seeds

*Malachite green		Neutral red	
log C_e	*log* q_e	*log* C_e	*log* q_e
1.479	1.627	1.924	1.470
2.001	1.719	2.250	1.511
2.291	1.714	2.414	1.573

*Example of calculation of Freudlich parameter:

For the adsorption of malachite green onto microwave-acid-alkali treated *Casuarina equisetifolia* seeds

$log\, q_e = log\, K_F + \frac{1}{n} log\, C_e$ (Freundlich equation)

$y = 0.1149x + 1.4653$ (Linear equation of Freundlich plot)

i) K_F, Freundlich constant

$log\, K_F = 1.4653$

$K_F = 29.2944$

ii) n, intensity of adsorption

$\frac{1}{n} = 0.1149$

$n = 8.7032$

APPENDIX E

KINETIC STUDY

i. Pseudo-first-order kinetic model

Table E.1: $\log (q_t - q_e)$ for raw *Casuarina equisetifolia* seeds

Dye	Malachite green			Neutral red		
Time, t (min)	200 mg/L	300 mg/L	400 mg/L	200 mg/L	300 mg/L	400 mg/L
5	1.2572	1.2839	1.2717	0.9519	1.0029	1.0563
10	1.2308	1.2723	1.2742	0.9311	1.0029	1.0524
15	1.1681	1.2578	1.2488	0.8375	0.9154	1.0399
20	1.1411	1.1992	1.1855	0.7642	0.8765	1.0297
25	1.1323	1.1072	1.1342	0.6977	0.8500	1.0013
30	1.0631	1.0594	1.1024	0.6515	0.8390	0.9340
60	0.9624	0.9018	1.0243	0.4945	0.5224	0.8744
90	0.8221	0.6977	0.9756	0.3788	0.3784	0.6942
120	0.6784	0.3744	0.8002	0.0662	0.0326	0.5550
150	0.2906	-0.5457	0.5012	-0.2420	-0.7320	0.2878
180	-0.4229	-1.0449	0.0271	-1.1136	-0.6190	-1.2548
210	-0.5343	-1.2864	-0.6401	-1.1468	-0.9821	-1.0264
240	-3.2924	-3.1938	-3.4150	-2.6739	-3.5076	-3.0576

Table E.2: $\log (q_t - q_e)$ for acid-alkali treated *Casuarina equisetifolia* seeds

Dye	Malachite green			Neutral red		
Time, t (min)	200 mg/L	300 mg/L	400 mg/L	200 mg/L	300 mg/L	400 mg/L
5	1.4385	1.5877	1.6231	1.1434	1.2195	1.3333
10	1.3972	1.5579	1.5854	1.1169	1.1380	1.3346
15	1.3676	1.5283	1.5841	1.0999	1.1084	1.3178
20	1.3449	1.5061	1.5579	1.0783	1.0878	1.3125
25	1.3172	1.4233	1.5403	1.0210	1.0620	1.2979
30	1.2980	1.4086	1.4935	1.0219	0.9930	1.2652
60	1.1236	1.2679	1.3383	0.8516	0.8813	1.1707
90	0.9648	1.0845	1.2313	0.6309	0.6296	0.9899
120	0.7922	0.9346	1.0767	0.4718	0.4326	0.7214
150	0.5063	0.6588	0.9308	0.3296	-0.2490	0.4738
180	0.0972	0.3816	0.5931	0.0500	-1.7328	-0.4662
210	-0.3077	-1.2580	-0.4063	-0.2102	-1.0949	-0.5096
240	-3.0368	-2.7905	-2.8641	-2.6383	-3.8500	-2.8447

Table E.3: $log\ (q_t - q_e)$ for microwave-acid-alkali treated *Casuarina equisetifolia* seeds

Dye	Malachite green			Neutral red		
Time, t (min)	*200 mg/L	300 mg/L	400 mg/L	200 mg/L	300 mg/L	400 mg/L
5	1.5528	1.6885	1.6829	1.3870	1.4174	1.5092
10	1.4848	1.6432	1.5995	1.3640	1.3495	1.4238
15	1.4256	1.5666	1.5021	1.3238	1.3119	1.3681
20	1.3918	1.5377	1.4570	1.2782	1.1842	1.2608
25	1.3505	1.5023	1.3950	1.2230	1.1138	1.1502
30	1.3181	1.4578	1.3373	1.1763	1.0706	1.1103
60	1.1376	1.1803	1.1463	0.9811	0.9382	1.0089
90	0.9191	0.9018	0.9434	0.8257	0.6978	0.8829
120	0.5368	0.4958	0.7530	0.5179	0.1545	0.6012
150	0.1686	0.4536	0.4233	0.2073	-0.1254	0.1351
180	-0.1021	0.2052	-0.1785	-0.4087	-0.7693	-0.9042
210	-0.1452	-0.6920	-0.6690	-0.5966	-0.8658	-0.8402
240	-4.1931	-2.9379	-3.2231	-3.4698	-3.2066	-3.0506

*Example of calculation of pseudo-first-order model parameter:

For the adsorption of 200 mg/L of malachite green onto microwave-acid-alkali treated *Casuarina equisetifolia* seeds

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad \text{(Pseudo-first-order model equation)}$$

$$y = -0.0155x + 1.9048 \text{ (Linear equation)}$$

iv) q_e, calculated (mg/g)

$log\ q_e$ = 1.9048

q_e = 80.32 mg/g

v) k_1, first-order-rate constant (min^{-1})

$-\frac{k_1}{2.303}t$ = -0.0155x

k_1 = 0.0357 min^{-1}

ii. Pseudo-second-order kinetic model

Table E.4: t/q_t for raw *Casuarina equisetifolia* seeds

Dye	Malachite green			Neutral red		
Time, t (min)	200 mg/L	300 mg/L	400 mg/L	200 mg/L	300 mg/L	400 mg/L
5	2.0086	2.5971	1.8586	3.5119	3.5758	9.1034
10	2.8108	4.1143	3.8710	5.4294	7.1515	9.9662
15	2.5667	4.9263	4.1077	4.2892	4.6376	12.9691
20	2.9714	3.7515	3.3028	4.3812	5.0753	13.4785
25	3.5671	2.9942	3.2196	4.6384	5.7005	13.6451
30	3.3310	3.0976	3.4378	5.0911	6.5759	14.4657
60	5.2634	4.5547	5.5505	8.2726	7.3750	15.0827
90	6.4601	5.5677	7.5430	11.2739	9.9175	15.2164
120	7.5943	6.3891	7.9614	13.0287	11.5529	16.2584
150	8.0569	7.1889	8.2356	15.3026	13.2983	16.5730
180	8.9143	8.5471	8.8580	17.4791	16.0362	16.9947
210	10.3562	9.9534	9.9263	20.1028	18.1516	17.5305
240	11.6672	11.3472	11.2230	23.1373	20.9338	20.1920

Table E.5: t/q_t for acid-alkali treated *Casuarina equisetifolia* seeds

Dye	Malachite green			Neutral red		
Time, t (min)	200 mg/L	300 mg/L	400 mg/L	200 mg/L	300 mg/L	400 mg/L
5	1.3333	1.8622	1.8210	1.2378	1.2509	7.5337
10	1.6027	2.0340	1.6027	2.0557	1.4628	7.2940
15	1.9024	1.6411	2.3613	2.7947	1.9380	8.0042
20	2.2049	1.7174	2.3255	3.3459	2.4000	8.4208
25	2.3951	1.9339	2.4920	3.3523	2.7656	8.6907
30	2.6466	2.1725	2.2100	4.0350	2.7947	9.0847
60	3.3508	2.8712	2.6157	5.5313	4.6275	9.8093
90	4.0953	3.2990	3.2494	6.5799	5.5169	11.0503
120	4.8000	3.8926	3.6586	8.0060	6.7162	13.4294
150	5.3592	4.3015	4.1433	9.4838	7.4958	16.1398
180	6.0107	4.8619	4.4105	10.6949	8.7564	16.8974
210	6.8392	5.3334	4.7364	12.1134	10.1668	19.7692
240	7.6932	6.0865	5.3657	13.3669	11.6647	28.7805

Table E.6: t/q_t for microwave-acid-alkali treated *Casuarina equisetifolia* seeds

Dye	Malachite green			Neutral red		
Time, t (min)	200 mg/L	300 mg/L	400 mg/L	200 mg/L	300 mg/L	400 mg/L
5	0.7520	1.4182	1.4182	0.9704	0.7955	0.9779
10	0.8454	1.1962	0.8372	1.5608	0.9930	0.9195
15	0.9544	0.9699	0.7524	1.7747	1.2583	1.0663
20	1.1290	1.1210	0.8669	1.8951	1.1664	1.0427
25	1.2533	1.2172	0.9300	1.9502	1.2863	1.0740
30	1.3914	1.2692	1.0011	2.0657	1.4518	1.2235
60	2.0954	1.6136	1.5914	3.0068	2.5256	2.2057
90	2.6423	2.0291	2.0964	3.9411	3.2795	3.0228
120	3.0832	2.4391	2.6060	4.5741	3.8706	3.5909
150	3.6685	3.0310	3.0575	5.3729	4.7347	4.1614
180	4.3298	3.5484	3.5262	6.1771	5.5797	4.8276
210	5.0424	4.0286	4.0780	7.1729	6.5028	5.6352
240	5.6654	4.5863	4.6413	8.1274	7.4007	6.4152

*Example of calculation of pseudo-second-order model parameter:

For the adsorption of 200 mg/L of malachite green onto microwave-acid-alkali treated *Casuarina equisetifolia* seeds

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{(Pseudo-first-order model equation)}$$

$$y = 0.0205x + 0.7029 \qquad \text{(Linear equation)}$$

i) q_e, calculated (mg/g)

$$\frac{t}{q_e} = 0.0205x \qquad \text{where, } t = x$$

$$q_e = 48.78 \text{ mg/g}$$

ii) k_2, second-order-rate constant (g/mg.min)

$$\frac{1}{k_2 q_e^2} = 0.7029 \qquad \text{where, } qe = 48.78 \text{ mg/g}$$

$$k_2 = 0.0357 \text{ g/mg.min}$$

iii) h, initial sorption rate (mg/g.min)

$$
\begin{aligned}
h &= k_2 q_e^2 \\
&= 0.0357 \text{ g/mg.min} \times 48.78 \text{ mg/g} \\
&= 1.410 \text{ mg/g.mg}
\end{aligned}
$$

LIST OF PUBLICATIONS

1. Anis Ayuni Aman Zuki, Mohamad Awang, Asmadi Ali @ Mahmud, Mohammad Hussin Zain, Jazulhafiz Jefri Jaafar. Adsorption of Malachite Green Dye on Microwave and Chemically Treated *Casuarina Equisetifolia* Seeds as an Eco-Friendly Adsorbent. ***Advances in Environmental Biology, 9(27),*** *216-223, 2015.*
2. Anis Ayuni Aman Zuki, Mohamad Awang, Asmadi Ali @ Mahmud, Mohammad Hussin Zain, Jazulhafiz Jefri Jaafar. Removal of neutral red dye from aqueous solution by raw and microwave-chemical modified coastal plant, *Casuarina equisetifolia* seeds as adsorbents. ***International Journal of Applied Chemistry, 12(1),*** *29-33, 2016.*
3. Anis Ayuni Aman Zuki, Mohamad Awang, Jazulhafiz Jefri Jaafar, Asmadi Ali @ Mahmud, Mohammad Hussin Zain. Equilibrium studies of malachite green dye adsorption on green adsorbent from *Casuarina equisetifolia* seeds. Will be published in ***Jurnal Teknologi***.

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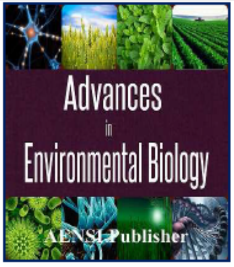

Adsorption of Malachite Green Dye on Microwave and Chemically Treated *Casuarina Equisetifolia* Seeds as an Eco-Friendly Adsorbent

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ABSTRACT

The use of abundantly available coastal plant, *Casuarina equisetifolia* seeds as an eco-friendly adsorbents in batch adsorption was investigated. The adsorption of Malachite green (MG) dye onto microwave and chemically treated *Casuarina equisetifolia* plant seeds was carried out in the influence of various parameters such as contact time, initial dye concentration and adsorbent dosage. The results show that the adsorption for both adsorbents reached equilibrium within 180 min. Microwave and chemically treated *Casuarina equisetifolia* seeds (MCR) are more effective than chemically treated *Casuarina equisetifolia* seeds (CR) for the removal of MG dye. The percentage of MG dyes removal increased with the decrease of dye concentration and increase of the contact time and adsorbent dosage. The highest MG dye removal for CR and MCR adsorbents using 1.0 g of adsorbent dosage was 93.53% and 95.95% respectively. The data of malachite green dye for both adsorbent fitted well with the Langmuir isotherm models, with good correlation coefficients $R^2 = 0.9554$ and $R^2 = 0.9851$ respectively. Therefore, the application of adsorbent from *Casuarina equisetifolia* seeds for the removal of MG dye was successfully demonstrated.

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Removal of neutral red dye from aqueous solution by raw and microwave-chemical modified coastal plant, Casuarina equisetifolia seeds as adsorbents

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Abstract - **This study investigated the potential of coastal plant, *Casuarina equisetifolia* seeds on the removal of cationic dye, neutral red in aqueous solution by batch adsorption experiments. Characterization of adsorbent was done by using scanning electron microscope (SEM), Fourier Transform infrared spectroscopy (FTIR) and TAPPI standards for surface morphology, surface functional groups and chemical composition, respectively. The studies were carried out under several parameters such as contact time, adsorbent dosage and initial dye concentration. The equilibrium adsorption for all experiments was achieved within 180 min. The percentage of dye removal increased with the increase of adsorbent dosage and contact time and the decrease of the initial dye concentration. The highest dye removal recorded at 1.0g for microwave-chemical modified *Casuarina equisetifolia* plant seeds was 94.39%. Equilibrium data were best presented by Freundlich model. It was observed that the correlation coefficient (R^2) and Freundlich constant (K_F) for microwave-chemical modified *Casuarina equisetifolia* plant seeds are 0.9791 and 3.677mg/g, respectively. The rate of adsorption, n, also indicated favourable nature of adsorption and a physical process.**

Keywords—Casuarina equisetifolia; neutral red; batch adsorption; isotherm

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