Biomass for Green Removal of Dyes

by

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15369

Dissertation submitted with partial fulfilment of

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Universiti Teknologi PETRONAS
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

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(Dr. Chew Thiam Leng)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgement, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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NUR ASIAH BINTI MOHD FAUZI

ABSTRACT

The expanding development of various industries in Malaysia had led to serious pollution to the environment. One of the industries is textiles industries. Disposal of waste water containing residual dyes from textile industries into river is one of the environmental issues nowadays. It is a very dangerous practice as the waste water contain chemicals that can pollute the water in the river. Hence, the waste water need to be treated before being disposed to the river nearby. There are many methods in removing dyes in waste water and can be categorized under three sections which are chemicals, physicals, and biological method. Adsorption method which falls under physical method had been chosen in this project as it is a simple and efficient method. Various agriculture wastes, biomasses had been studied s adsorbent for adsorption method in removing dyes. By researches in recent years, biomass is readily available abundantly and environment friendly. In this project, corn silk was studied as the adsorbent in removal of Janus green dye. The effect of the parameters which are biomass loading, dye concentrations, and solution pH on the dye adsorption using corn silk was investigated. The biomasses also we characterized using four analytical techniques which are Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), and also Thermogravimetric Analysis (TGA).

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my deepest gratitude to the following persons who has made the completion of this Final Year Project to be possible. First and foremost I would like to thank both of my parents for supporting me throughout this year of study and hardship in finishing this project. They had always supported me in either in terms of encouragement and even financial state. Without them, it is quit hard to finish this project.

Special thanks to my supervisor, Dr. Chew Thiam Leng for guiding me throughout this Final Year Project. He had guided me from the beginning of the project until the submission of the final report. I am very lucky to have him as my supervisor. I would also like to thank the examiners and also coordinators for both Final Year Project 1 and Final Year Project 2 for guiding and spending lots of their times on us either in allocating the best time for presentation and also giving briefings. Not to forget the lab technicians whose continuously monitoring us during experiment until we finish. Last but not least, I would like to thank my friends for supporting me directly or indirectly. May Allah repays all your kind deeds in this world or hereafter.

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CHAPTER 1
INTRODUCTION

1.1 Background

Textiles industry represents an important sector to Malaysian economic where coloured textiles grow continuously day by day according to the growth of population providing a new dimension to Malaysian economic.

The wastewaters discharge from textiles industries includes residual dyes. Since dyes are not bio-degradable, therefore untreated dyes may cause water pollution and serious threat to the environment. In order to reduce the threats to the environments, different methods have been applied to remove dyes from the wastewaters. The technologies for dye removal can be divided into three categories: biological, chemical and physical (Robinson et al., 2001). Biological methods include fungal decolourization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems. These methods are commonly used as many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants. Coagulation or flocculation combined with flotation and filtration, precipitation-flocculation with Fe(II)/Ca(OH)2, electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes are the processes under chemical methods. For physical method, that includes membrane – filtration processes (nanofiltration, reverse osmosis, electrodialysis) and adsorption techniques. This project will be focusing on the adsorption techniques for removal of dyes.

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid onto a surface. This process creates a film of the adsorbate on the surface of the adsorbent. Adsorption techniques had been widely used in removal of dyes using different adsorbents. Such adsorbents are activated carbon, natural or synthetic zeolites, natural clay minerals, silica gel and activated aluminium, biomass, and silicic acid. However, there are some restrictions in using these techniques. The problems that arise when using these adsorbents are some of the adsorbents are too expensive, less effective, not exists in abundance and etc. Adsorption techniques using biomass had been continuously expending as biomass giving out low cost but effective adsorption.

Biomass is biological material derived from living, or recently living organisms. In the context of biomass for energy this is often used to mean plant based material, but biomass can equally apply to both animal and vegetable derived material. In terms of adsorption techniques in removal of dyes, biomass includes the wastes from other industries such as palm wastes, coconut frond, corn silk, banana stalk, and many more. This project focusses on removal of dyes using biomass adsorption. Some of the advantages of using biomass are its abundant existence, low cost and, technical effectiveness. Most of the biomass can be found in abundance from palm, coconut, banana, bamboo, corn, and others wastes. This adsorption using biomass is to utilize those plants even its wastes. This will be very cost effective and helpful to reduce the wastes produced by those industries.

1.2 Problem Statement

Removal of dyes from wastewater is very important to the environment. To keep environment safer from pollutions, various alternatives had been created to reduce the pollutions. Few alternatives include biological, chemical and physical methods. Under these three method, technologies involved includes adsorption, oxidation, flocculation coagulation, membrane filtration, biological treatment, and etc. The existence of these processes shows that many alternatives had been done to save the environment.

However, there are obstacles faced by each method that leads to the creation of more alternatives. Problems faced by biological method are in term of technical constraint. Biological treatment requires large land area and is constrained by sensitivity towards divernal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Further, biological treatment is incapable of obtaining satisfactory colour elimination with current conventional biodegradation processes (Robinson et al., 2001). Although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin (Ravi Kumar et al., 1998).

Besides, there are also problems brought by chemical method. Chemicals always relate with expensive price and possibility that secondary pollution will arise due to excessive chemical. This is common problems where high electrical demand and consumption of chemical reagents. For physical methods, problems always relate with the membrane process. This process has limited lifetime before membrane fouling occurs and cost of periodic replacement must include in any analysis of their economic viability. Among all the technologies exist, adsorption had been chosen as it is simple and more improvement had been done to make this process useful.

Under adsorption techniques, numerous numbers of adsorbents had been used to remove dyes from wastewater. Examples of adsorbents are activated carbon, zeolites, silicic acid, natural clay minerals, and etc. All these adsorbents have their own advantages and disadvantages. Some of the adsorbents are quite expensive but effective and some are less expensive but not very effective. However, most of the problems faced by some of the adsorbents are not environmental friendly, and also do react with chemicals in the water.

Another alternative adsorbent used in adsorption process is biomass. The adsorption using biomass keep growing nowadays and various researches had been done on different biomass. Some of the benefits of biomass are environmental friendly as biomass comes as wastes from other industries such as agriculture and also low cost as it is already exists in abundance. Adsorption using biomass also considered as green technology as this process does not react other chemicals or change the properties when mixed with wastewater containing chemicals. So, the adsorption using biomass using corn silk had been chosen in this project.

1.3 Objectives

There are 3 objectives for this project:

1) To study the adsorption capacity of Janus Green Dye using corn silk.
2) To characterize the raw biomass using different analytical techniques.
3) To investigate the effect of adsorption parameters on the Janus Green Dye removal using raw biomass.

1.4 Scope of Study

The study for removal of dyes using biomass begins with the utilisation of corn silk from the stalls nearby the university area. The corn silks were collected and processed into biomass materials to be used for dye removal. The biomass was used for the adsorption process. Three parameters were investigated which are pH reading, biomass loading, and also dye concentration for its effect on Janus Green removal using corn silk.

The results gained were analysed. Calculation of amount sorption of dye, adsorption equilibrium and also percentage of dye removal were calculated. The calculated data was analyzed and discussion. The project was completed by thesis writing.

CHAPTER 2
LITERATURE REVIEW

2.1 Dye Removal

2.1.1 Type of Dye

Removal of dyes is gaining increasing popularity among researchers due to the rapid development of textiles industry nowadays. Textiles industry gives off wastewater that containing different types of dyes that are harmful for the environment. Since dyes are non-biological, the water containing those dyes could affect the environment and also living organisms in the water.

There are several ways in classifying dyes. Dyes can be classified according to the source of materials, chemical class of the dyes-based on the nature of their respective chromospheres, nuclear structure, industrial classes and also application. Usually, dyes are classified according to its application. It is convenient to use the application classification used by the US International Trade Commission for application classes. Table 2.1 shows the classification of dyes according to U.S. International Trade Commission.

Table 2.1: Classification of dyes according to U.S. International Trade Commission (Austin, George T., 789)

Class of Application	**Description**
Acid	Derived the name from their insolubility in acid baths. Used for dyeing protein fibres such as wool, silk, and nylon. Usually the dyes are azo, triaryl methane, or anthraquinone complexes.
Basic	Basic dyes are mostly amino and substituted amino compounds soluble in acid and made insoluble by solution being made acid. Most are triarylmethane or xanthenes. These can be used to dye wool or cotton with a mordant, but are usually used for duplicator inks, and carbon paper
Direct	Direct dyes are used to dye cotton directly, that is, without the addition of a mordant. They are also used to dye union goods (mixed cotton, and wool, or silk). These are generally azo dyes and their solubility in the dye bath is often reduced by adding salt.
Disperse	Modern synthetics (cellulose acetate, plastics, polyesters) are difficult to dye. Disperse dye applied as very finely divided materials which are adsorbed onto the fibres with which they then form a solid solution. Simple, soluble azo dyes can be used, but insoluble anthraquinone colors are best and most common. Both penetrate the fibre.
Reactive	These dyes react to form a covalent link between the dye and the cellulosic fibre which they are customarily used to dye. This produces goods of outstanding wash-resistance. Cotton, rayon, and some nylons are dyed by this, the newest type of dyestuff to be invented (1956)

The dye that will be used in this experiment is Janus Green dye. Based on the reading made, there are fewer experiments that used Janus Green dye. So, the dye will be changes to Janus Green dye for this experiment. Janus Green dye also falls under basic type category.

2.1.2 Dye Removal Technologies

There are several technologies in order to remove dyes from wastewater. The technologies include physical, chemical, and biological method. For physical method, there are membrane-filtration and also adsorption. Coagulation, electroflotation, and also electrokinetic coagulation includes under chemical method. Lastly, for biological method there are funga decolourization, microbial degradation and also adsorption using (living or dead) microbial biomass. All of the methods have the advantages and also disadvantages. Table2.2 below shows the advantages and disadvantages of physical and chemical methods of dye removal from industrial effluent (Robinson, 2011).

Table 2.2: Advantages and disadvantages of physical and chemical methods of dye removal from industrial effluent (A. Latif Ahmad et al., 2002)

Category	Physical/Chemical Method	Advantages	Disadvantages
Chemicals	Fentons reagent	Effective decolourisation of both soluble and insoluble dyes	Sludge generation
	Ozonation	Applied in gaseous state: no alteration of volume	Short half –life(20 min)
	Photochemical	No sludge production	Formation of by-product
	NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amine

	Cucurbituril	Good sorption capacity for various dyes	High cost
	Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
	Irradiation	Effective oxidation at lab scale	Requires lots of dissolved O_2
	Elektrokinetic coagulation	Economically feasible	High sludge production
	Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Physical	Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
	Membrane filtration	Remove all dye types	Concentrated sludge production
	Activated carbon	Good removal of wide variety of dyes	Very expensive
	Peat	Good adsorbent due to cellular structure	Specific surface area for adsorption are lower than activated carbon
	Wood chips	Good sorption capacity for acid dyes	Requires long retention times

2.2 Adsorption Techniques

Among all these techniques of removing dyes, adsorption techniques are one of the most effective ways to remove dye. The adsorbents can be classified into two types which are natural and also synthetic adsorbents. Some of the examples of adsorbents under natural adsorbents are natural clay, natural zeolites, biomass and etc. Synthetic adsorbents include activated carbons, polymers & resins, activated alumina, silica gel, synthetic zeolites and etc. Using these adsorbents, the adsorption process becomes one of the effective ways to remove dyes. Table 2.3 shows the examples of natural and synthetic dyes.

Table 2.3: Classification of natural and synthetic adsorbents

Natural Adsorbent	**Synthetic Adsorbent**
Natural clay Natural Zeolites Biomass	Activated carbons Polymers & resins Activated alumina Silica gel Synthetic zeolite

From all the adsorbents stated, biomass is one of the potential adsorbents to be used. Some of the advantages of biomass adsorbents are low cost, environmental friendly, and effective. It is said to be low cost as biomass already exists in abundant especially from other industries. The waste from the other industries which is the biomass could be utilised by making it as the adsorbent for dye removal. Biomass is also effective although it is not as effective as other adsorbent. It still can absorb the dye and save the environment. It is also environmental friendly as it biological material and did not react with other substances in the water.

2.2.1 Adsorption using Biomass

Biomasses are mostly found from agriculture waste. Some of the plantation produces many types of biomass for example palm tree. The palm tree could be used as biomass from the leaves to the trunks and even its wastes. A single plant could produce a lot of biomass for adsorption used. Examples of biomass are empty coconut brunch, banana stalk, coconut frond, oil palm frond, bamboo leave, corn silks, and etc. Various researches had been done to identify the adsorption of biomass on removal of dyes using different biomass produced.

Research on adsorption using biomass had been done by many researches. The biomass includes rice husk, pine leaves, raw mango seed, tea wastes, and etc. All these biomass are wastes that will not be used by any processes. Instead of throwing away the raw biomass, they are being used to helps in adsorption of dye. Table 2.4 shows the biomass and dyes used in past researches together with the references.

Table 2.4: Biomass and dyes used in past researches

Biomass	**Dye**	**Refferences**
Rice Husk	Malachite Green	Ramaraju B, et al. 2013
Pine leaves	Methylene Blue	Yagub MT, et al. 2012
Raw mango seed	Methylene Blue	Senthil Kumar P, et al. 2013
Sugarcane bagas se	Rhodamine B	Zhang Z, et al. 2013
Peanut husk	Indosol Black	Sadaf S, Bhatt HM. 2013
Tea waste	Acid Orange 7	Khosla E, et al. 2013
Cashew nutshells	Congo Red	Senthil Kumar P, et al. 2010
Waste mixtures	Methylene Blue	Amran M, et al. 2011

CHAPTER 3
METHODOLOGY

3.1 List of equipment and chemicals

3.1.1 List of Chemicals and Biomass

Table 3.1 shows the list of chemicals and biomass used in the experiment.

Table 3.1: List of chemicals and biomass

Chemical	**Biomass**
Hydrochloric Acid (HCl) Sodium Hydroxide (NaOH)	Corn Silk

3.1.2 List of Apparatus and Glassware

Table 3.2 shows the list of apparatus and glassware used in the experiment.

Table 3.2: List of apparatus and glassware

Apparatus	**Glassware**
Ultraviolet-Visible (UV-Vis) Grinder Siever Shaker pH meter	Volumetric Flask Beaker Conical Flask Measuring Cylinder Spatula Disposable Pipette Syringe

3.2 Project Methodology

Figure 3.1 shows the process flow of the project from the beginning till the end of Final Year Project. Starting with literature review, all the works and research done by former researchers were studied before starting the experiment. Step two was the identification of biomass, chemicals, and also apparatus needed. This is important before starting the experiments. Selection of biomass is important to avoid using the same biomass from previous experiments. Corn silk was selected as there is no study on corn silk adsorption of dye yet.

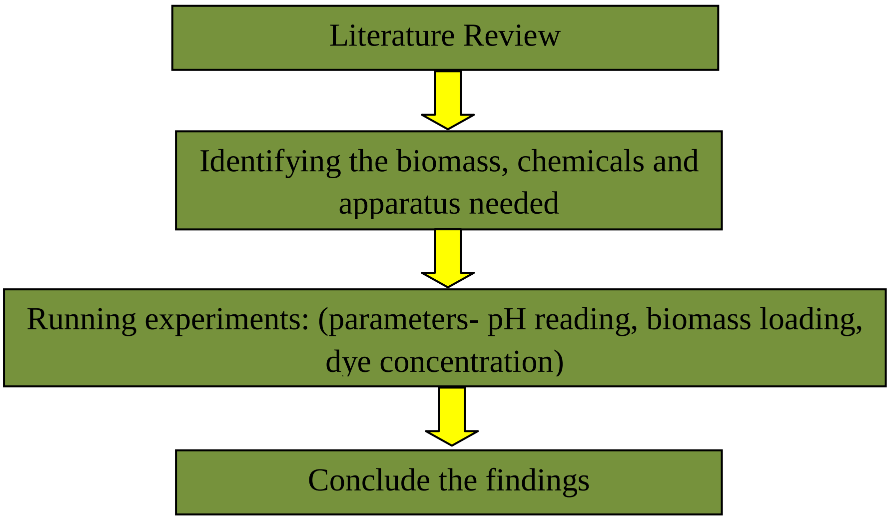

FIGURE 3.1 Process flow of the project

Running the experiment was the step after identifying the equipment needed for the experiment. The next step was analysing result. By the end of the experiment, conclusion was made in terms of effectiveness of the biomass chosen on the dye removal. The result of the findings would help in the conclusion part.

3.3 Experimental Procedures

3.3.1 Preparation of Biomass

1. Corn silk had been collected from the nearest source which is at the fruit stall or night market in Seri Iskandar area.
2. The collected corn silks were sun dried for one day.
3. The sun dried corn silk then been grinded using grinder.
4. The grinded corn silk then been soaked in hot distilled water for a few times.
5. The corn silk had been dried in a hot oven with a temperature of 60^{o}C for 24 hours.
6. The dried corn silks were sieved using siever.

3.3.2 Adsorption Studies

1. Dye solution had been prepared by mixing the required amount of Janus Green dye with the distilled water to produce stock solution of 500mg/L.
2. The stock solution then been segregated in few conical flasks to be used in different parameter.
3. The biomass loading had been adjusted by using different mass of biomass, to be ranged from 1 g/L to 9 g/L.
4. The dye concentrations were adjusted from 100 mg/L to 500 mg/L
5. The pH of the solutions was adjusted by adding HCl to get more acidic and NaOH to get more alkaline solution.
6. The range of pH reading ranged from 2 to 6.
7. Table 3.3 shows the reading range of all parameter

Table 3.3: Range of every parameter

Parameter	**Range**
pH reading	2-6
Biomass Loading	1.0 g/L - 9.0 g/L
Dye Concentration	100 mg/L- 500 mg/L

8. For the first parameter which is biomass loading, the conical flasks with the biomass loading of 1 g/L had been put in a shaker and agitated with a speed of 200 rpm.
9. Sample of the solution had been taken for every 10 minutes starting from the first conical flask until the last one.
10. For every sample taken, the concentration had been analysed using Ultraviolet-Visible (UV-Vis).
11. Steps 8 until 10 had been repeated using other biomass loading which are 3 g/L, 5 g/L, 7 g/L, and 9 g/L.
12. Then, steps were repeated using different parameter which are pH reading and dye concentration.
13. Based on the concentration obtained, the amount of sorption at time *t*, q_t (mg/g) had been calculated.

3.3.3 Adsorption Capacities

All the equations involved in the determining the adsorption capacities had been shown below. The equation had been used to analyze the results and finding the isotherm.

The amount of sorption at time *t*, q_t (mg/g), is calculated by:

$$q_t = \frac{(C_o - C_t)V}{M} \qquad \text{....................... Eq 3.1}$$

Where Ct (mg/L) is the liquid-phase concentration of dye at any time.

The amount of adsorption at equilibrium, q_e (mg/g)

$$q_e = \frac{(C_o - C_e)V}{M} \qquad \text{....................... Eq 3.2}$$

The percentage of dye removal:

$$\%C = \frac{(C_o - C_e)}{C_o} x100 \qquad \text{……………………} \quad \text{Eq 3.3}$$

3.5 Characterization Techniques

3.5.1 Scanning Electron Microscope (SEM)

SEM model Pro X, brand Phenom was used as a method for high-resolution imaging of surfaces. The SEM used electrons for imaging, much as light microscope uses visible light. The function of SEM was to evaluate the surface morphology of the sample.

3.5.2 X-Ray Diffraction (XRD)

XRD model D8 Advance, brand Bruker was used for a wide variety of material characterization studies. Primarily, the technique identifies crystalline species in a material.

3.5.3 Thermogravimetric analysis (TGA)

TGA model Pyris 1, brand Perkin Elmer was a method of thermal analysis in which changes in physical and chemical properties of materials were measured as a function of increasing temperature or as a function of time. TGA is used to measure the thermal stability of the sample.

3.5.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR model 8400s, brand Shimadzu was a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collected high spectral resolution data over a wide spectral range.

3.6 Gantt Chart and Key Milestone

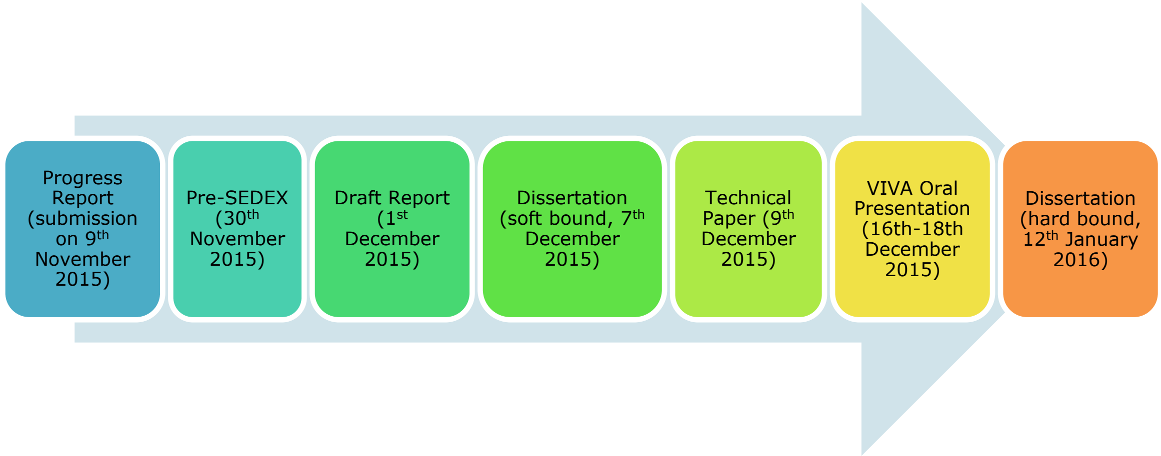

FIGURE 3.2 Key Milestone for FYP 2

The key milestone showed the important dates during FYP 2. The submission of dissertation is the middle stage for FYP 2. Few important dates could be seen based on the chart given. Then, there will be submission of technical paper and VIVA oral presentation in the middle of December. Then there will be the submission of dissertation hard bound on 12th January 2016 which is the last stage in FYP 2. During the stage, the report must be completed and follow the correct format according to the FYP guidelines.

NO	WEEK DETAILS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	17
1	Running the experiment															
2	Preparation of Progress Report															
3	Submission of Progress Report															
4	Preparation for Pre-SEDEX presentation															
5	Continuation of the Project															
6	Preparation of Dissertation report															
7	Pre-SEDEX Presentation															
8	Submission of Draft Report															
9	Submission of Dissertation (soft bound)															
10	Submission of Technical Paper															
11	VIVA Oral Presentation															
12	Submission of Dissertation (hard bound)															

The Gantt chart shows the flow of FYP 2 for the second semester. There total of 12 important tasks need to be done according to the Gantt chart. Now, the submission of dissertation is coming to the final phase of the FYP 2. This report need to be submitted on Week 12 for softcopy and after final exam for hardbound. The experiment had been finish and now there are still few analysis needed to be done to be put in the report. The experiment had run smoothly with the guidance from the supervisors and the course coordinator. The project will be finished once the hard bound been submitted.

CHAPTER 4
RESULTS AND DISCUSSIONS

4.1 Characterization Techniques

4.1.1 Fourier Transform Infrared (FTIR)

FTIR is one of the characterization techniques that are used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. In this project, corn silk sample had been sent for characterization using FTIR. The sample tested comprises of corn silk before adsorption and after adsorption of Janus green. The objective is to detect the difference occurred on the corn silk after adsorbing the Janus green dyes.

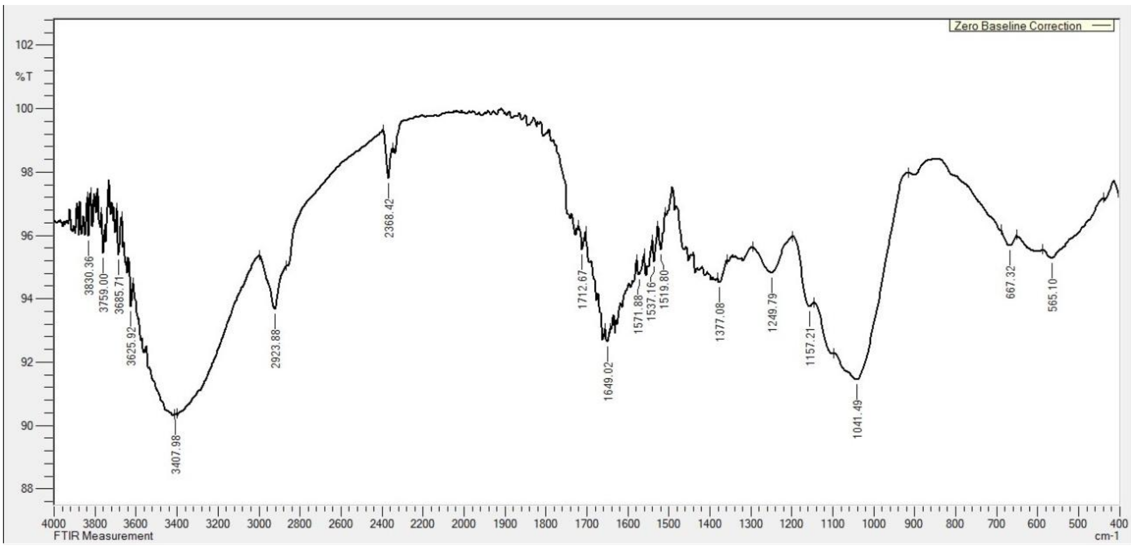

FIGURE 4.1   IR-Spectra for corn silk sample before adsorption

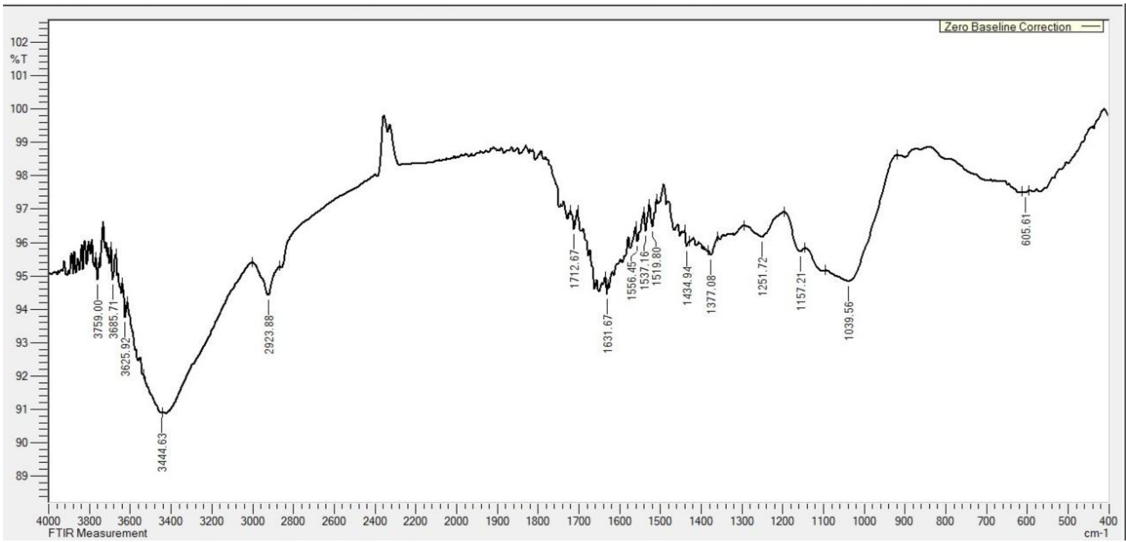

FIGURE 4.2 IR-Spectra for corn silk sample after adsorption

Based on the graphs shown above, there are few differences between the corn silk before and after adsorption. The peaks did not have the same value before and after but still in the range of the same type of bond. There is also peak that vanished after the adsorption happened. Table 4.1 shows the value of the peak before and after with the type of bonds that exists.

Table 4.1: Peak value and type of bonding

No	Peak Value(cm-1)		Type of Bonding
	Before	After	
1	3407.98	3444.63	OH & NH Stretching, C-H Stretching
2	2923.88	2923.88	C-H Stretching
3	2368.42	-	C≡X C=X=Y Stretching
4	1649.02	1631.67	C=O Stretching, C=N Stretching
5	1041.49	1039.56	C-O Stretching, C-N Stretching, C-C Stretching

There are 5 min peaks that had been selected to be analysed. For the first peak that is ranged from 3000 cm-1 to 3500 cm-1 indicates the existence of OH & NH Stretching, C-H Stretching bonds in the sample. The next peak is ranged from 2800 cm-1 to 3000 cm-1 indicates the existence of C-H Stretching in the sample. For wavelength from 1600 cm-1 to 1800 c-1 shows the presence of C=O Stretching, C=N Stretching bonds in the component. C-O Stretching, C-N Stretching, and C-C Stretching existence can be proved from the peaks ranged from 1000 cm-1 to 1200 cm-1. However, there was a peak that disappeared after adsorption happened. Peak 2368.2 cm-1 shows the presence of C≡X C=X=Y Stretching bonding in the corn silk sample before adsorption and the peak was disappeared after adsorption happened.

4.1.2 Thermogravimetric Analysis

The next characterization method was TGA where it is used as a method of thermal analysis in which changes in physical and chemical properties of materials were measured as a function of increasing temperature or as a function of time. TGA is used to measure the thermal stability of the sample. The same corn silk sample before and after were sent to be analysed. The figure below shows the graph of total weight loss for both conditions.

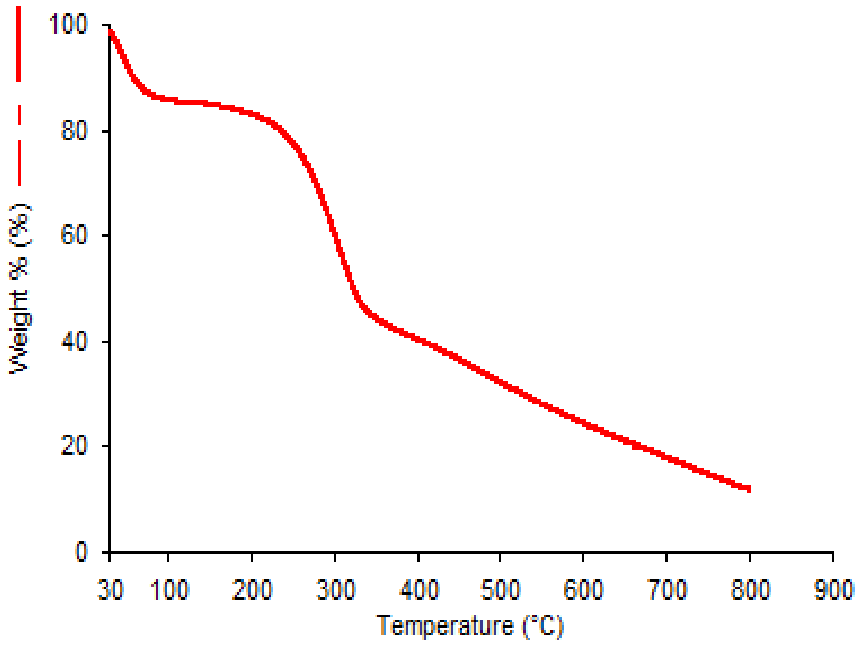

FIGURE 4.3 Total weight loss of corn silk sample before adsorption

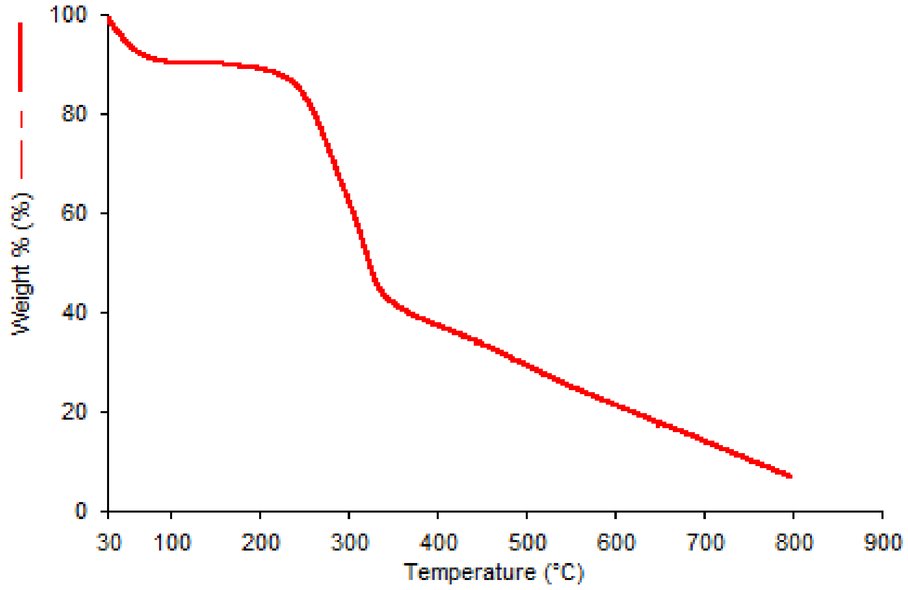

FIGURE 4.4 Total weight loss of corn silk sample after adsorption

Based on the graph obtained, the total weight loss of both sample could be determine. The percent of weight loss for corn silk before adsorption is 88.3 % while weight loss after adsorption is 93.14 %. This shows that the weight loss after adsorption is higher than before adsorption. Both graphs also shows similar trend of decreasing. There are three phase of decreasing which are from 0^{o}C to 60^{o}C then constant and decrease again from 230^{o}C until 330^{o}C. Then, from the temperature, the weight loss continued decreasing until the temperature of 800^{o}C.

4.1.3 Scanning Electron Microscope (SEM)

The last characterization is scanning electron microscope. It is a type of electron microscope that produces images if a sample by scanning it with a focused beam of electron. SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The figure below shows the images of the surface of corn silk using different magnification for before and after adsorption.

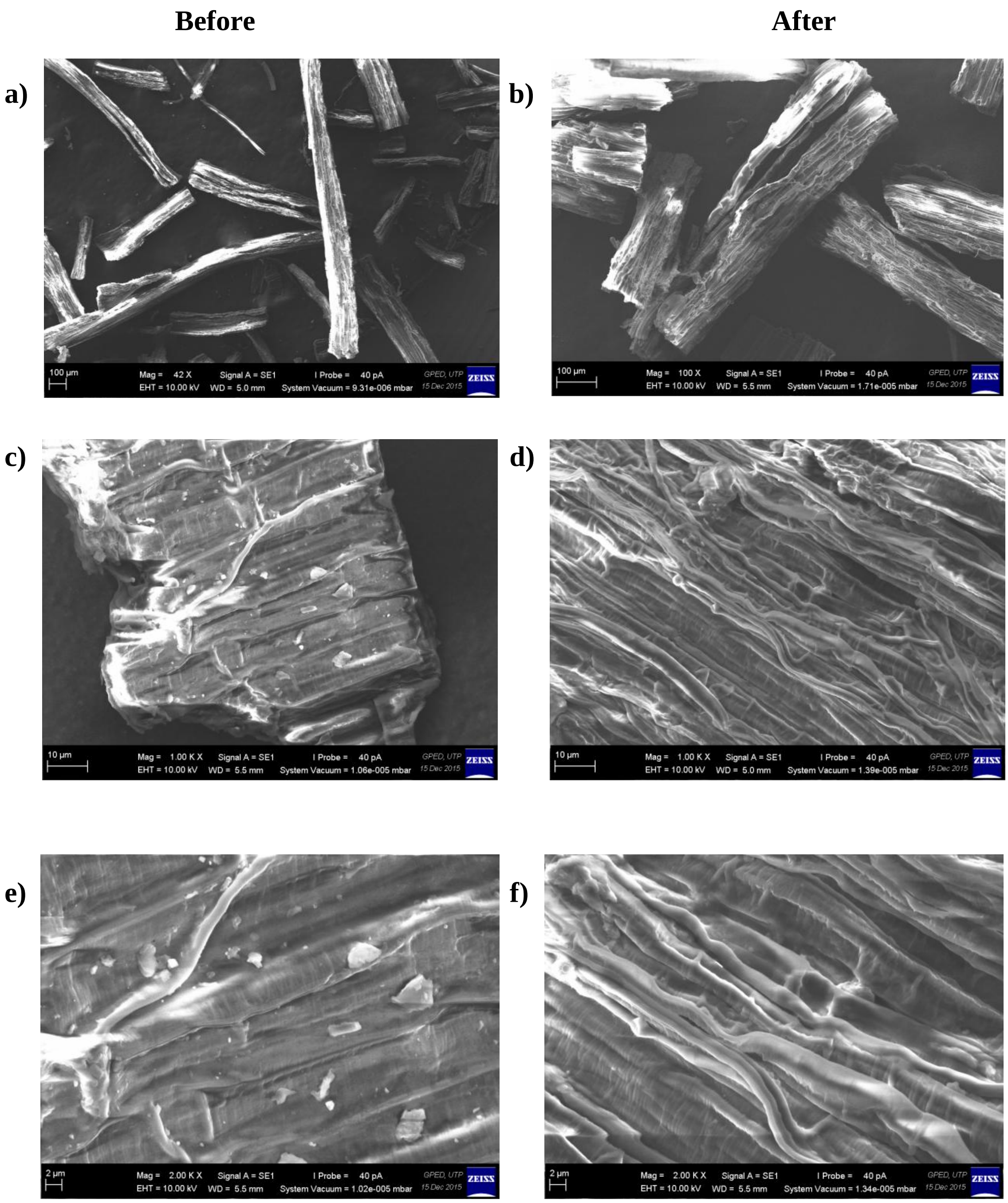

FIGURE 4.5 SEM images of (a) raw corn silk (100µm); (b) after adsorption (100µm); (c) raw corn silk (10µm); (d) after adsorption (10µm); (e) raw corn silk(2µm); (f) after adsorption (2µm)

Corn silk has a coarse surface morphology with a large number of channels (Figure 4.5 a-d). These micron size channels appear to be dominant features in CS morphology. However, on (Figure 4.5 a-d) can be seen that corn silk appears to have low porosity, which is typical for raw biomaterials.

Based on these facts, it is safe to say that nano pores of corn silk do not play significant role in Janus Green dyes adsorption and that observed micro channels might be responsible for good adsorption characteristics of the material. These channels allow the diffusion of ions in Janus Green dyes, and thus provide more active sites for metal ion adsorption on the interior and exterior of the CS. On the surface of CS after Janus Green adsorption, aggregates of lead are not visible indicating absence of micro-precipitation (Figure 4.5 (b,d,f)). It is also noticeable that the surface of the CS has become porous and that delamination of the material has occurred.

4.2 Janus Green Dyes Adsorption

4.2.1 Biomass Loading

To study the effect of biomass loading on the rate of dye adsorption onto corn silk, the experiments were carried out using the fixed concentration but with different adsorbent dose which are 1g/L, 3 g/L, 5 g/L, 7 g/L, and 9 g/L. Based on the results obtained, it is found that the adsorption capacity is inconsistent from 1 g/L to 9 g/L. This may be due to few errors that might happen during handling the experiment. Table 4.2 shows the adsorption capacity reading for biomass loading from 1 g/L to 9 g/L.

Table 4.2: Adsorption capacity for each biomass loading

Biomass Loading (g/L)	**Adsorption Capacity (mg/g)**
1	38000
3	4500
5	6400
7	3214.286
9	2333.333

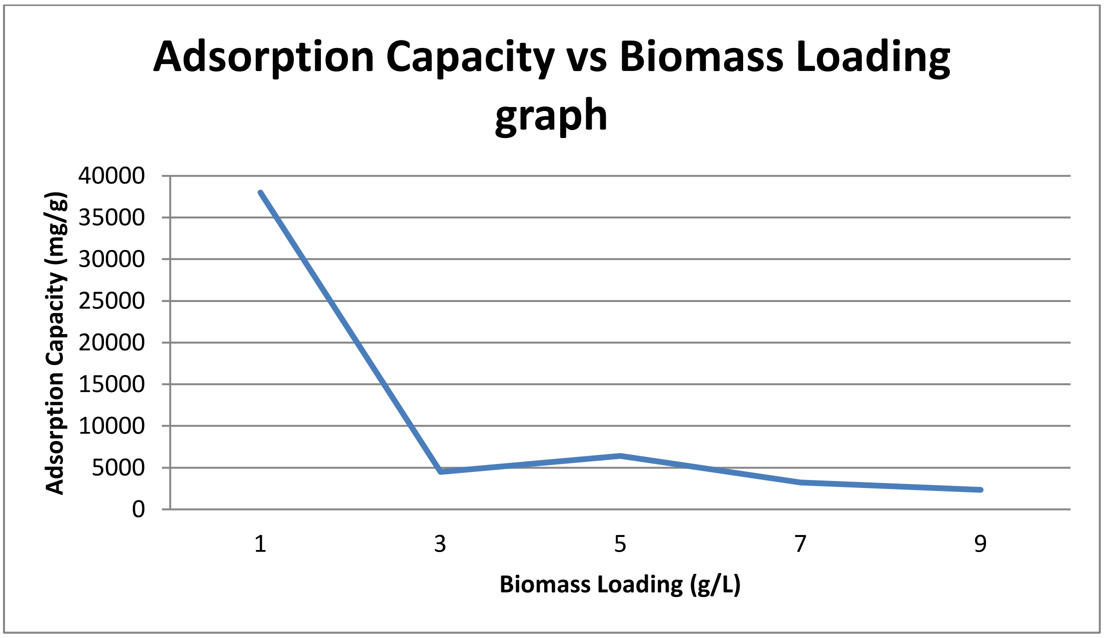

FIGURE 4.6 Adsorption capacity vs biomass loading graph

Based on the graph obtained, the trend shows drastic declination of adsorption capacity reading from 1 g/L to 3 g/L followed by slight increase to 5 g/L and then decrease again for 7 g/L and 9 g/L. The unusual trend of the graph shows that there might be some errors or flaws during the experiment. The adsorption capacity reading should be increasing with the increase in biomass loading.

Few errors can be identified during the experiment such as human errors and dilution error. Human errors might be because of the eye is not level with the liquid in measuring cylinder and also problems during dilution as the ratio for the dilution is 1:99 where 1 is the dye concentration and 99 is the distilled water. Hence, slight different in the measurement of dye concentration would also effect the reading of uv- vis. Besides, the dyes may be degraded after a few days being mixed with distilled water. The degradation of dyes will cause the adsorption capacity also decrease. Furthermore, the increase in biomass also could affect the adsorption capacity as too much of biomass will cause the accumulation of biomasses in the solution and made the solution did not clear enough for uv-vis to test. Hence, these errors must be reduced while doing the experiment so that acceptable graph could be obtained and clear explanation can be done.

4.2.2 Dyes Concentration

In this project, the dyes concentration parameter involves the different concentration of initial dye concentration. The concentration used in this project are 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, and 250 mg/L. Based on the results obtained, it is found that the amount of Janus Green adsorb increase with the increase of initial dye concentration. Table 5.2 shows the absorption capacity reading of the final sample for each concentration which after being shakes for 100 minutes.

Table 4.3: Adsorption Capacity reading or each dyes concentration

Dye Concentration (mg/L)	Adsorption capacity (mg/g)
50	6400
100	15400
150	18700
200	31900
250	39200

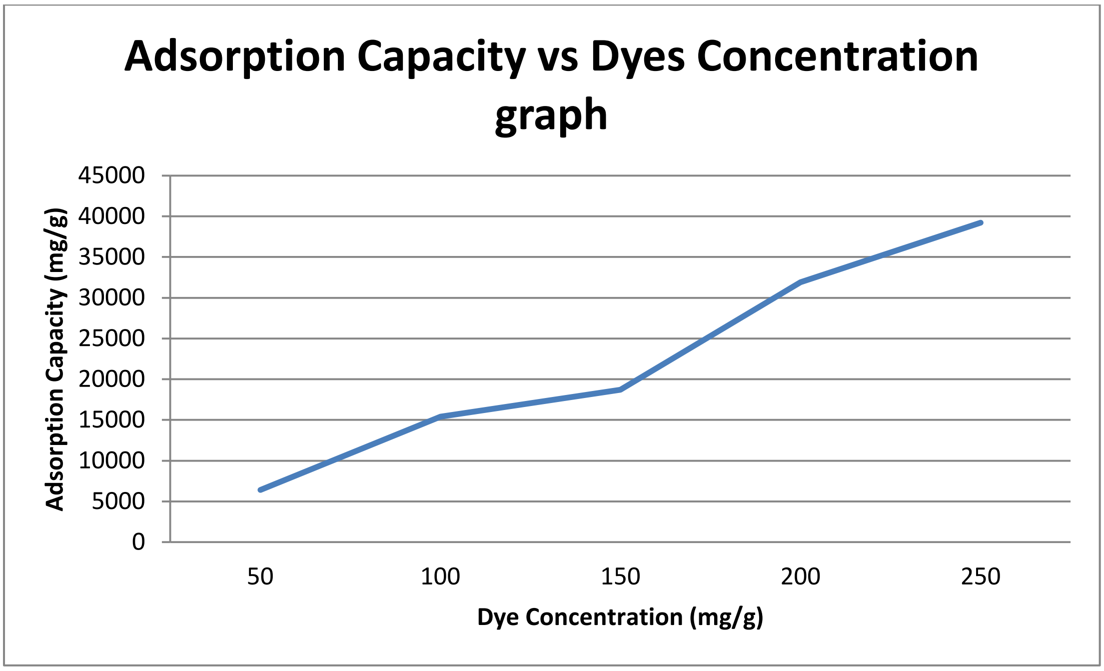

FIGURE 4.7 Adsorption Capacity Vs Dye Concentration Graph

The above graph shows adsorption capacity vs dyes concentration graph that was obtained from experiment that had been done. Based on the graph, it is shown that the higher the initial dye concentration the higher the adsorption capacity. The readings for adsorption keep increasing from 6400 mg/g to 39200 mg/g for concentration of 50 mg/L to 250 mg/L. The initial Janus Green dye concentration provides an important driving force to overcome all mass transfer resistance (Amran et al., 2011). This is also due to the saturation of the adsorption sites at higher dye concentrations (Ozer et al., 2007). Hence, it can be said that the higher initial dye concentration will enhance the adsorption process.

4.2.3 Solution pH

The pH factor is very important in adsorption process. The magnitude of electrostatic charges will be controlled by pH of medium which imparted by ionized dye molecules. As a result the rate of adsorption will vary with pH of aqueous medium (Onal et al., 2006). In this project, the effect of pH was determined by having three different solution pH but with the same dye concentration and biomass loading. The dye concentration used was 300 mg/L and 5 g/L of biomass loading.

The effect of pH on the removal of Janus green dye was shown in the figure 4.7 for three solution pH which are 2, 4, and 6. There was only three solution pH that had been tested due to the time constraint for this project. However, the optimum pH had been obtained among the three reading tested. Table 4.4 shows the adsorption capacity for each solution pH.

Table 4.4: Adsorption capacity or each solution pH

Solution pH	**Adsorption Capacity (mg/g)**
2	1000
4	2400
6	1300

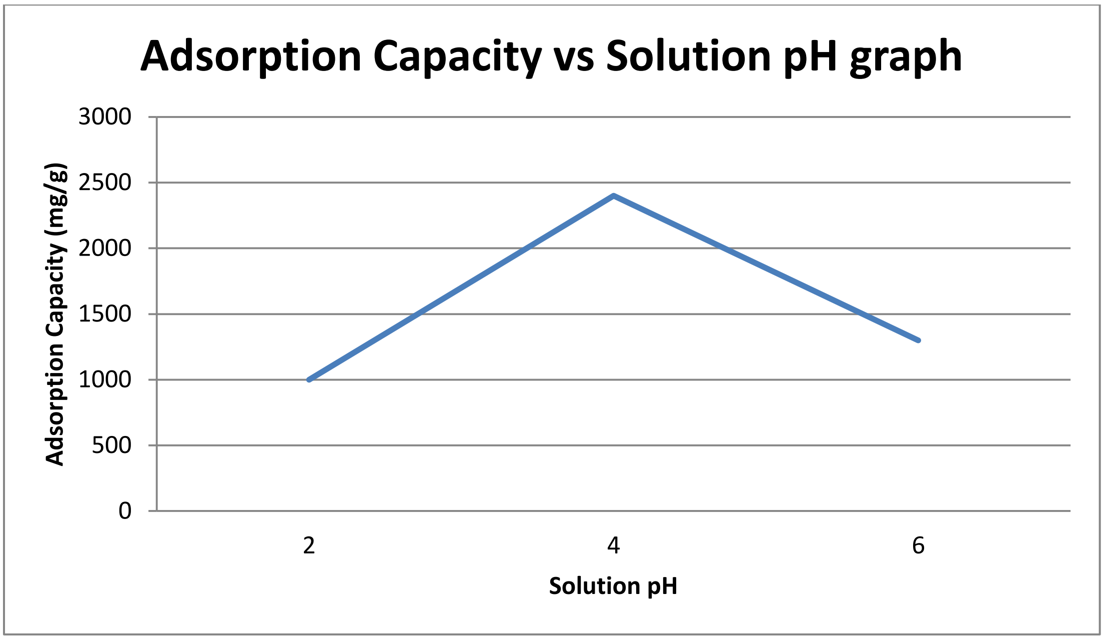

FIGURE 4.8   Adsorption Capacity vs solution pH graph

Based on the graph, it is shown that the highest value for adsorption capacity is under pH 4. The value of adsorption capacity for pH 2 is 1000 mg/g and increased to 2400 mg/g for pH 4 and decreased back to 1300 mg/g for pH 6. This showed that the optimum pH for the adsorption of Janus green using corn silk is at pH 4. The lower adsorption of dye at low pH is because the adsorbent surface may get positively charged due to the presence of H^+ ions excess as a result competing with the cation groups on the dye for adsorption sites, while at higher solution Ph, the adsorbent surface may get negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction (Amran et al., 2011). At the higher pH, the dye removal decrease and this may be due to hydrolysis of adsorbent surfaces, which create positively charged sites (Hamdaoui, 2006).

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Based on all the information provided, adsorption is one of the techniques in removing dye from waste water. The production of biomass in abundance helped in adsorption process of dye. This will reduce the amount of biomass being sent to disposal centre. Utilisation of biomass had bring many benefits for example, environmental friendly, green technology, and also cost effective. Further research should be done to investigate the ability of each biomass in adsorption process.

In current project, the Janus Green adsorption using corn silk was studied using three different parameters. The first parameter that had been studied is biomass loading. Based on theory, the higher the biomass loading, the higher the adsorption capacity that happened. However, in this current project, it is found that the reading of the adsorption capacity is not constant and could not get smooth graph. Few analysis had been done to find the causes and relevancies of the results obtained. The second parameter is dye concentration. In this project, it is found that the higher the dye concentration, the higher the adsorption capacity obtained. This is because of more dyes that could be adsorbed when the concentration is higher. The last parameter that had been tested is solution pH. There are three solution pH that had been tested which are 2, 4, and 6. Based on the results obtained, it is found that solution pH of 4 has the highest adsorption capacity among the three readings. This indicates that pH 4 is the optimum condition for adsorption of Janus green using corn silk to happen.

Besides that, the corn silk samples before and after adsorption also were sent for characterization. The characterizations chosen were Fourier Transform Infrared (FTIR), Thermogravimetric Analysis (TGA), and also Scanning Electron Microscope (SEM). The samples were sent before and after adsorption in order to find the difference that happened on the corn silks after adsorption happened. As a conclusion, this project could prove that corn silk is also a good adsorbent for adsorption process and also as a green technology available nowadays.

5.2 Recommendations

There are few recommendations that can be done to improve the accuracy of the experiment. It is important to follow the right step in order to make the experiment successful. Below are the following recommendations that can be done:

1. The time range to test the samples using UV-Vis from the first sample to another should not be too short and also too long in order to get proper plot of graphs.
2. Improve on the handling techniques so that the graphs obtained would be smooth and easy to be analysed
3. Include the isotherm study in the project to get the equilibrium adsorption and produce more results.
4. Include the kinetic study by analysing the effect of temperature towards the adsorption capacity of the corn silk on Janus green.
5. Add more parameter to find the optimum condition for the adsorption to happen such as temperature, rpm, and others.
6. Do experiments on the adsorption capacity of corn silk that had ben dried using different temperature.
7. Determine the maximum capacity of corn silk needed before doing the experiment.

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APPENDICES

Calibration Curve

Before starting the experiment, a calibration curve needs to be done to obtain the result for concentration. Calibration curve of absorbance versus concentration is compulsory so that the reading can be read through the calibration curve. The concentration that had been used to make calibration curve is from 50 mg/L to 500 mg/L. Table 6.1 and Figure 6.1 shows the calibration curve obtained from the experiment, with correlation coefficient, R^2 of 0.9906.

Table 6.1: Readings for Calibration Curves

Standard ID	Concentration(mg/L)	Analyte	Residual	Ordinate
1. Standard	50	79.1322	-29.1322	0.0618
2. Standard	100	117.8845	-17.8845	0.068
3. Standard	150	142.0937	7.9063	0.0719
4. Standard	200	177.0008	22.9992	0.0775
5. Standard	250	214.7252	35.2748	0.0835
6. Standard	300	297.5933	2.4067	0.0968
7. Standard	350	337.5222	12.4778	0.1032
8. Standard	400	395.4232	4.5768	0.1124
9. Standard	450	470.6614	-20.6614	0.1245
10. Standard	500	517.9635	-17.9635	0.132

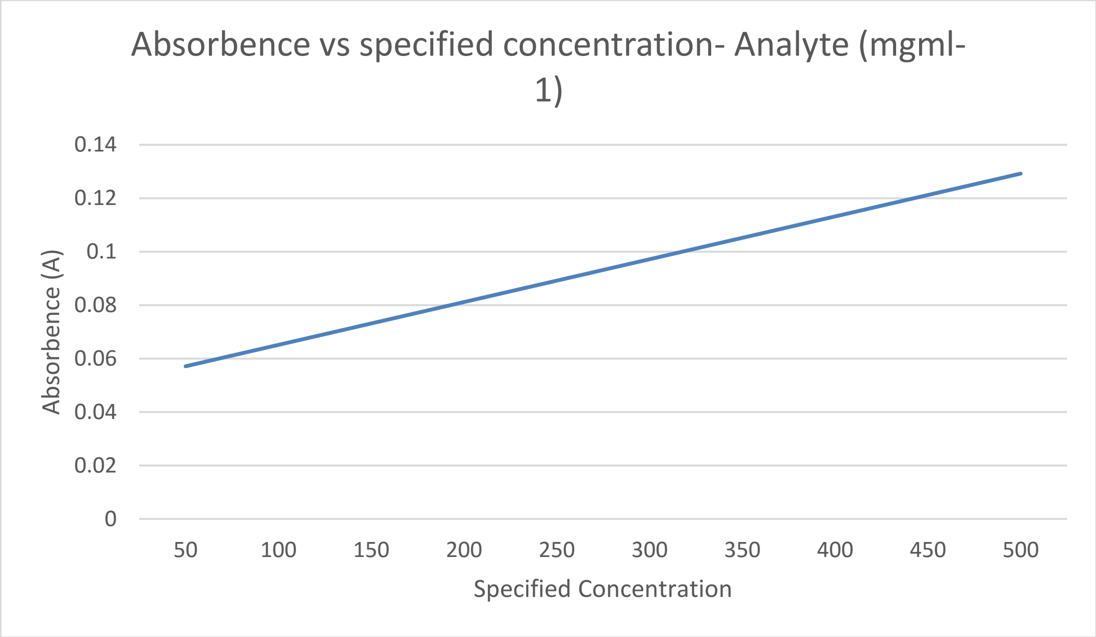

FIGURE 6.1 Calibration Curve