SYNTHESIS OF MODIFIED COFFEE GROUND ADSORBENTS TO REMOVE MALACHITE GREEN DYES

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SYNTHESIS OF MODIFIED COFFEE GROUND ADSORBENTS TO REMOVE MALACHITE GREEN DYES

by

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ACKNOWLEDGEMENT

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TABLE OF CONTENTS

ACKNOWLEDGEMENT ........................................................................................................... 2
TABLE OF CONTENTS ........................................................................................................... 3
LIST OF TABLES ................................................................................................................... 7
LIST OF FIGURES ................................................................................................................ 9
LIST OF SYMBOLS .............................................................................................................. 11
LIST OF ABBREVIATIONS ................................................................................................... 12
LIST OF APPENDICES ......................................................................................................... 13
ABSTRAK .............................................................................................................................. 14
ABSTRACT ............................................................................................................................. 16

CHAPTER 1  INTRODUCTION ................................................................................................. 17
1.1 Background of Study .................................................................................................... 17
1.2 Problem Statement ...................................................................................................... 21
1.3 Objectives ..................................................................................................................... 22
1.4 Scope of Study .............................................................................................................. 23
1.5 Organization of Thesis ................................................................................................. 23

CHAPTER 2  LITERATURE REVIEW ..................................................................................... 25
2.1 Water Pollution from Textile Industry ........................................................................ 25
   2.1.1 Dyes ...................................................................................................................... 27
   2.1.2 Classification of Dyes .......................................................................................... 28
   2.1.3 Malachite Green .................................................................................................. 29
2.2 Technology for Wastewater Treatment ...................................................................... 30
   2.2.1 Treatment of Dye Wastewater ........................................................................... 31
   2.2.2 Treatment (Physical/Chemical) ......................................................................... 31
   2.2.3 Adsorption .......................................................................................................... 32
2.3 Adsorbent ...................................................................................................................... 32
2.3.1 Biomass-based Adsorbent ................................................................. 33
2.3.2 Coffee Waste as Adsorbent ............................................................... 36
2.4 Optimization using Response Surface Methodology ................................. 37
2.4.1 Central Composite Design (CCD) ....................................................... 38
2.5 Factors Affecting Rate of Adsorption .................................................... 39
2.5.1 pH .................................................................................................. 39
2.5.2 Contact Time .................................................................................... 40
2.5.3 Temperature ..................................................................................... 41
2.5.4 Initial Dye Concentration ................................................................. 41
2.5.5 Adsorbent Dosage .......................................................................... 42
2.6 Characterization of Biomass-based Adsorbent .......................................... 42
2.6.1 Surface Area Analysis (BET) ............................................................. 43
2.6.2 Surface Morphology Analysis (SEM) ................................................. 44
2.6.3 Elemental Analysis (CHNS) ............................................................... 45
2.6.4 Surface Chemistry Analysis (FTIR) .................................................. 45
2.7 Adsorption Isotherms (Equilibrium Studies) ............................................ 46
2.7.1 Langmuir Isotherm ........................................................................ 47
2.7.2 Freundlich Isotherm ....................................................................... 48
2.7.3 Temkin Isotherm ............................................................................ 48
2.8 Adsorption Kinetics (Kinetic Studies) .................................................... 49
2.8.1 Pseudo-First-Order Kinetic Model .................................................... 50
2.8.2 Pseudo-Second-Order Kinetic Model .............................................. 51

CHAPTER 3 METHODOLOGY ................................................................. 52
3.1 Materials and Equipment ...................................................................... 52
3.1.1 Chemicals and Reagents Required ................................................... 52
3.1.2 Equipment and Instrumentation Required ....................................... 53
3.2 Flow Chart of Methodology .................................................................. 54
CHAPTER 4 RESULTS AND DISCUSSION ................................. 66

4.1 Calibration Curve .................................................................. 66

4.2 Preliminary Study .................................................................. 67

4.3 Model Fitting Response Surface Methodology (RSM) .......... 69

4.3.1 Statistical Analysis of Percentage of MG Dye Removal using MCG .................................................. 71

4.3.2 Effects of Parameters on Malachite Green Dye Removal Efficiency .......................................................... 75

4.3.2(a) Interactive Effect of pH of MG Dye Solution and Contact Time .......................................................... 76

4.3.2(b) Interactive Effect of pH of MG Dye Solution and Adsorbent Dosage of MCG ........................................ 77

4.3.2(c) Interactive Effect of Contact Time and Adsorbent Dosage of MCG ....................................................... 79

4.3.3 Statistical Analysis of Adsorption Capacity of MCG ...... 80

4.3.4 Effects of Parameters on Modified Coffee Ground Adsorbent Efficiency ..................................................... 83
4.3.4(a) Interactive Effect of pH of MG Dye Solution and Contact Time ......................................................... 85

4.3.4(b) Interactive Effect of pH of MG Dye Solution and Adsorbent Dosage of MCG ........................................... 86

4.3.4(c) Interactive Effect of Contact Time and Adsorbent Dosage of MCG ....................................................... 87

4.3.5 Optimization of Process Parameters using Desirability Function ...................................................................... 88

4.4 Characterization of Modified Coffee Ground Adsorbent ................................................................. 91

4.4.1 Surface Area Analysis (BET) .................................................................................................................. 91

4.4.2 Surface Chemistry Analysis (FTIR) ....................................................................................................... 93

4.4.3 Surface Morphology Analysis (SEM) .................................................................................................... 95

4.4.4 Elemental analysis (CHNS) ................................................................................................................ 97

4.5 Batch Adsorption Study .......................................................................................................................... 98

4.6 Linear Isotherm Modelling ..................................................................................................................... 100

4.7 Linear Kinetic Modelling ....................................................................................................................... 102

4.8 Sustainability ........................................................................................................................................ 104

CHAPTER 5 CONCLUSION AND RECOMMENDATION ........................................... 106

5.1 Conclusion ........................................................................................................................................... 106

5.2 Recommendation .................................................................................................................................. 108

REFERENCES ............................................................................................................................................ 109

APPENDICES ............................................................................................................................................ 118
LIST OF TABLES

Table 2.1 Physicochemical properties of malachite green dye. [Adapted from (Raval, 2017; Ojediran et al., 2020)] ................................................................. 30

Table 2.2 Comparison of the adsorption capacity of various adsorbent to remove MG dye. ........................................................................................................... 34

Table 2.3 BET surface area and textural properties of coffee waste adsorbent. [Adapted from (Wong, 2020)] ........................................................................ 43

Table 2.4 Functional groups of coffee waste and spent coffee ground. [Adapted from (Anastopoulos, 2017)] ............................................................... 46

Table 3.1 List of chemicals and reagents used in the experiment...................... 52

Table 3.2 List of equipment and instrumentation used in this experiment. ......... 53

Table 3.3 Coded Values of the independent variables. ..................................... 59

Table 3.4 Design matrix obtained from Design Expert using central composite design. ........................................................................................................ 60

Table 4.1 Preliminary study of different types of chemical used to treat coffee ground. ........................................................................................................... 68

Table 4.2 Matrix of independent variables and responses. .............................. 70

Table 4.3 Fit Statistics of percentage MG dye removal analysis model. .......... 73

Table 4.4 ANOVA shows the quadratic surface model's accuracy in predicting percentage dye removal using MCG....................................................... 74

Table 4.5 Fit Statistics of adsorption capacity of MCG analysis model. .......... 82

Table 4.6 ANOVA shows the quadratic surface model's accuracy in predicting adsorption capacity of MCG................................................................. 83

Table 4.7 Optimum and experimental data for the optimized condition.......... 91

Table 4.8 BET surface area of different samples of coffee ground adsorbent........ 92
Table 4.9 Comparison of elemental composition of different coffee ground samples. .......................................................... 98

Table 4.10 Isotherm model parameters by linear regression analysis.................. 101

Table 4.11 Kinetics model parameters for Malachite green dye adsorption........... 103
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>Industries that are responsible for the contribution of dye effluents in environment. [Adapted from (Katheresan, 2018)]</td>
<td>19</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>Water pollution from textile industry in several countries. [Adapted from (Paraschiv, 2015)]</td>
<td>26</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>The structure of the malachite green. [Adapted from (Raval, 2017)]</td>
<td>29</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Coffee ground. [Adapted from (Le et al., 2021)]</td>
<td>37</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>SEM images of coffee waste adsorbent at (a) 300x and (b)1500x, modified coffee waste adsorbent at (c) 300x and (d)1500x and foreign particles in (e) coffee waste and (f) modified coffee waste. [Adapted from (Wong, 2020)]</td>
<td>44</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Flow Chart of Final Year Project Activities</td>
<td>54</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Experimental setup for the chemical modification of coffee ground.</td>
<td>56</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>Calibration curve of MG dye solution at different concentration.</td>
<td>67</td>
</tr>
<tr>
<td>Figure 4.2</td>
<td>Predicted versus actual data for the percentage of Malachite Green dye removal using MCG.</td>
<td>75</td>
</tr>
<tr>
<td>Figure 4.3</td>
<td>3D response surface shows the effect of pH and contact time (hrs) for the percentage of malachite green dye removal using MCG.</td>
<td>76</td>
</tr>
<tr>
<td>Figure 4.4</td>
<td>3D response surface shows the effect of pH and adsorbent dosage (g) for the percentage of malachite green dye removal using MCG.</td>
<td>78</td>
</tr>
<tr>
<td>Figure 4.5</td>
<td>3D response surface shows the effect of contact time (hrs) and adsorbent dosage (g) for the percentage of malachite green dye removal using MCG.</td>
<td>79</td>
</tr>
<tr>
<td>Figure 4.6</td>
<td>Predicted versus actual data for the adsorption capacity of MCG adsorbent.</td>
<td>84</td>
</tr>
<tr>
<td>Figure 4.7</td>
<td>3D response surface shows the effect of pH and contact time (hrs) for the adsorption capacity of MCG.</td>
<td>85</td>
</tr>
</tbody>
</table>
Figure 4.8 3D response surface shows the effect of pH and adsorbent dosage (g) for the adsorption capacity of MCG. .................................................................................. 86

Figure 4.9 3D response surface shows the effect of contact time (hrs) and adsorbent dosage (g) for the adsorption capacity of MCG ......................................................... 88

Figure 4.10 Ramp of desirability by numerical optimization for the three major parameters of optimized parameters for MG removal and MCG adsorption capacity. ........................................................................................................ 89

Figure 4.11 FTIR spectra of raw CG adsorbent (sample A), MCG treated with chemical (sample B), MCG treated with chemical and heat (sample C) and MCG adsorbent after MG dye removal (sample D)......................... 93

Figure 4.12 SEM images of raw coffee ground (a,b), coffee ground with chemical treatment (c,d), coffee ground with chemical and heat treatment (e,f) and MG adsorbed coffee ground (g,h) ........................................ 95

Figure 4.13 Adsorption capacity of modified coffee ground versus contact time at various MG dye concentrations. ................................................................. 98

Figure 4.14 Freundlich isotherm plot for Malachite green dye adsorption........... 100

Figure 4.15 Pseudo second order linear kinetic model plot for Malachite green dye removal. ........................................................................................................ 102
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>L</td>
<td>Litre</td>
</tr>
<tr>
<td>mL</td>
<td>Milliliter</td>
</tr>
<tr>
<td>M</td>
<td>Molarity</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>w/v</td>
<td>Weight per volume</td>
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<tr>
<td>μm</td>
<td>Micrometer</td>
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<tr>
<td>%</td>
<td>Percentage</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
</tbody>
</table>
### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANOVA</td>
<td>Analysis of Variance</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller (BET)</td>
</tr>
<tr>
<td>CCD</td>
<td>Central Composite Design</td>
</tr>
<tr>
<td>CG</td>
<td>Coffee Ground</td>
</tr>
<tr>
<td>CV</td>
<td>Coefficient of Variation</td>
</tr>
<tr>
<td>df</td>
<td>Degree of freedom</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopic</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric Acid</td>
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<tr>
<td>MCG</td>
<td>Modified Coffee Grounds</td>
</tr>
<tr>
<td>MG</td>
<td>Malachite Green</td>
</tr>
<tr>
<td>MIP</td>
<td>Mercury Intrusion Porosimetry</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyethylenimine</td>
</tr>
<tr>
<td>rpm</td>
<td>Rounds per minute</td>
</tr>
<tr>
<td>RSM</td>
<td>Response Surface Methodology</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopic</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>Appendix</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
</tr>
<tr>
<td>A</td>
<td>Raw and Modified Coffee Ground</td>
</tr>
<tr>
<td>B</td>
<td>Equipment and Instrumentation Required</td>
</tr>
<tr>
<td>C</td>
<td>Calibration Curve</td>
</tr>
<tr>
<td>D</td>
<td>Preliminary Study</td>
</tr>
<tr>
<td>E</td>
<td>Experimental Data Sets Based on Runs Generated by RSM</td>
</tr>
<tr>
<td>F</td>
<td>Percentage of MG Dye Removal</td>
</tr>
<tr>
<td>G</td>
<td>Adsorption Capacity of MCG</td>
</tr>
<tr>
<td>H</td>
<td>Validation of Experiment</td>
</tr>
<tr>
<td>I</td>
<td>Characterization of Modified Coffee Ground Adsorbent</td>
</tr>
<tr>
<td>J</td>
<td>Batch Adsorption Study</td>
</tr>
<tr>
<td>K</td>
<td>Linear Isotherm Modelling</td>
</tr>
<tr>
<td>L</td>
<td>Linear Kinetic Modelling</td>
</tr>
</tbody>
</table>
SINTESIS PENJERAP SERBUK KOPI YANG DIUBAH SUAI UNTUK MENGHILANGKAN PEWARNA HIJAU MALACHITE

ABSTRAK

Sisa kopi yang dirawat dengan kalium hidroksida dan asid hidroklorik digunakan sebagai penjerap kos rendah untuk penjerapan larutan pewarna hijau malachite. Kajian awal dilakukan dan serbuk kopi dirawat dengan kalium hidroksida dan asid hidroklorik dengan rawatan haba telah menunjukkan peratusan penyingkiran pewarna hijau malachite tertinggi iaitu 96.14 % dan kapasiti penjerapan 23.51 mg/g bagi serbuk kopi yang diubah suai. Pengoptimuman parameter operasi untuk penyediaan penjerap serbuk kopi yang diubah suai untuk penyingkiran molekul pewarna hijau malachite telah dijalankan dengan menggunakan reka bentuk komposit pusat. Sebanyak 20 set eksperimen disimulasikan untuk mendapatkan parameter proses yang optimum bagi kajian ini. Berdasarkan hasil metodologi permukaan tindak balas, keadaan optimum untuk semua parameter berjaya dikenal pasti seperti pada pH 7.3, masa hubungan 6.9 jam dan dos penjerap 0.2 g, sementara peratusan maksimum penyingkiran pewarna hijau malachite yang diperoleh dari keadaan yang dioptimumkan adalah 85.02 % dan penjerapan kapasiti 1.65 mg/g. Sampel serbuk kopi telah dicirikan menggunakan Brunauer – Emmett – Teller (BET), spektroskopi inframerah transformasi Fourier (FTIR), mikroskopik elektron imbasan (SEM) dan penganalisis CHNS. Serbuk kopi yang telah diubah suai menunjukkan hasil pencirian yang lebih baik berbanding dengan serbuk kopi yang tidak dirawat. Kesan kepekatan awal pewarna, masa hubungan, pH larutan dan dos penjerap untuk penjerapan pewarna hijau malachite telah diselidiki untuk kajian keseimbangan dan kinetik. Model garis sesuhu Freundlich didapati sesuai digunakan untuk menjelaskan tingkah laku penjerapan perwarna hijau malachite dan plot model urutan kedua semua adalah sesuai dengan
pemerhatian eksperimen menggunakan analisis regresi linear. Kajian ini menunjukkan bahawa sisa kopi merupakan penjerap kos rendah yang berpotensi dan cekap untuk penyingkiran larutan pewarna hijau malachite.
SYNTHESIS OF MODIFIED COFFEE GROUND ADSORBENTS TO REMOVE MALACHITE GREEN DYES

ABSTRACT

Coffee waste treated with potassium hydroxide (KOH) and hydrochloric acid (HCl) was used as a low-cost adsorbent for the adsorption of malachite green (MG) dye solution. A preliminary study was carried out and the coffee ground treated with KOH and HCl with the heat treatment showed the highest MG dye removal percentage of 96.14% and 23.51 mg/g of adsorption capacity of MCG. Optimization of the operating parameters for preparation of modified coffee ground adsorbent for the removal of MG dye molecules using central composite design (CCD). A total of 20 set of experiment were simulated to get the optimum process conditions of this study. Based on the RSM results, the optimum conditions for all the parameters were successfully identified such at pH 7.3, contact time of 6.9 hours and adsorbent dosage of 0.2 g while the maximum percentage of MG dye removal obtained from the optimized condition was 85.02% and adsorption capacity of 1.65 mg/g respectively. The CG samples has been characterized using by Brunauer–Emmett–Teller (BET), Fourier transform infrared spectroscopic (FTIR), scanning electron microscopic (SEM) and CHNS analyser. MCG showed a better characterization result compared to untreated CG. The effect of initial concentration of dye, contact time, solution pH and adsorbent dosage for adsorption of MG dye has been investigated for equilibrium and kinetic study. Freundlich isotherm model was found perfectly fitted model to explain the adsorption behaviour of MG adsorption and pseudo second order model plot was best fitted with the experimental observation by using linear regression analysis. This study shows that CG waste showed a promising and efficient low cos adsorbent for the removal of MG dye solution.
CHAPTER 1
INTRODUCTION

The potential of modified coffee grounds (MCG) as a low-cost adsorbent to remove malachite green (MG) from aqueous solutions was investigated in this study. In order to study the effect of adsorption capacity of the adsorbent, there are four parameters were analysed in this project: pH, temperature, contact time and initial dye concentration of malachite green dye. In addition, to improve the operational parameters, the Response Surface Methodology (RSM) was used. Furthermore, the modified coffee ground adsorbent was characterized using four different methods of analysis: Brunauer–Emmett–Teller (BET) analysis, Scanning Electron Microscopic (SEM) analysis, Thermogravimetric Analysis (TGA), and Fourier Transform Infrared (FTIR) spectroscopy analysis.

1.1 Background of Study

Water pollution is becoming one of the major threats facing by all of our human being, animals and aquatic creatures. In the last few years, it was increased rapidly and reached the alarming levels. There are abundant of factors which can contribute for water pollution such as industrial waste, oil spillage, household and agricultural waste. The industrial effluents waste which are discharged without any proper treatments are one of the major sources of water pollution. This is due to some of the irresponsible industries that dispose unwanted effluents directly to the river. A report by United Nations Educational, Scientific and Cultural Organization (UNESCO) (2017) shows about 80 % of global wastewater is discharged to environment without any adequate treatments. In addition, the industrial effluents disposed may contain unwanted pollutants which included, synthetic hazardous dyes originating from a wide range of
industries for instance, pharmaceutical, cosmetic paint, textile, carpet, plastic, pulp and paper industries (Katheresan et al., 2018; Krishna Murthy et al., 2019a; Wong et al., 2020).

Dyes are known as chemical compounds which have abundant of uses in the industries such as for colouring purposes. Dyes can be divided into two types such as natural and synthetic dyes. The high demand for the dyes drive to the production of approximately around $7 \times 10^5$ tonnes of colouring from $1 \times 10^5$ commercially available dyes are manufactured each year (Katheresan, 2018). Unfortunately, dyes will be dumped into environmental water bodies without being treated once they have lost their properties.

Figure 1.1 illustrated five significant industries that are responsible for the presence of dye effluents in the environmental water bodies. Based on Figure 1.1, it shows that the highest amount of dye effluents is realized by the textile industries roughly about 54 % to the environment. The wastewater contains dye effluents discharged from these industries mentioned above are detrimental to human being, aquatic creatures and animals. Consequently, synthetic dyes can cause various health effects such as dermatitis, eczema and vasco-circulatory problems. Synthetic dyes also can interfere the penetration of sunlight and delay the photosynthetic activities (Krishna Murthy et al., 2019). Dyes which have carcinogenic, mutagenic and poisonous properties pose a serious hazard to aquatic life and water consumers (Saleh Bashanaini, 2019). Hence, a proper treatment of wastewater containing dyes are essential to preserve the river and environment from pollution.
There are various types of dye available according to its structure and properties. Dyes are classified into three main types of dyes which are cationic (basic dye), anionic (direct, reactive, acid dyes) and non-ionic (dispersive dyes). Basically, from all these dyes, cationic dyes are reported more toxic and brighter in colour compared to anionic dyes (Sukla Baidya et al., 2021). This research studies were focusing on the removal of malachite green dye which is known as one of the basic dyes presents in the wastewater. Malachite green (MG) dye is one of the cationic dyes which are present in the industrial effluents. MG is a high demand dye which comprises of abundant uses in industries. However, it gives several health effects to humans as well as aquatic and terrestrial animals (Raval et al., 2017). Due to the high content of MG dye in wastewater, a proper treatment method is needed before it is discharged to environment.

There are a few techniques used to remove dyes contaminants from the wastewater namely, coagulation, membrane filtration, ion exchange, adsorption and oxidation (Sukla Baidya, 2021). For the removal of dyes from industrial effluents, adsorption is a well-developed and cost-effective approach (Krishna Murthy et al.,

Figure 1.1 Industries that are responsible for the contribution of dye effluents in environment. [Adapted from (Katheresan, 2018)]
This approach is an efficient method due to its ease of process and operation, design simplicity, unreactive properties to toxic substance and also it can associate the removal of pollutants completely rather than breaking down to hazardous intermediates products. Activated carbon is a conventional adsorbent with a high adsorption capacity that is used abundantly in the industries for the wastewater treatment. However, commercial activated carbon is very expensive to be used in industrial scale (Krishna Murthy et al., 2019).

As a consequence of this, biomass-based wastes are used to synthesize adsorbents in order to replace the commercial activated carbons. The biomass wastes are cheap, cost-effective, environmental friendly and it is readily available in huge amount (Krishna Murthy et al., 2019). These types of biomass-based waste are renewable source and can be found in unlimited amount. This can help to reduce the environmental pollution as well where wastes are utilized properly. There are several agro-based materials are used as potential low-cost adsorbent such as wheat straw, peanut husks, rice straw, rice husks, fruit peel, tea waste, coffee husks, sawdust and sugarcane bagasse are used for the removal of dye-containing wastewater in the industries (Baldikova et al., 2015). However, the biomass-based wastes need to undergo further modification with chemicals in order to enhance the performances characteristics of adsorbents (Wong, 2020).

Coffee waste is one of the extensively used biowastes for the synthesis of low-cost adsorbents. Coffee waste is abundantly found due to the high number of coffee consumers globally. According to total coffee production of exporting countries, approximately 168.84 million tonnes of coffee is produced globally in 2019/2020 (International Coffee Organization (ICO)). Besides, roughly 10.29 million tonnes of
coffee are exported globally in January 2020 (International Coffee Organization (ICO)). This shows that the production will continue to rise due to the increasing domestic consumption of coffee. Besides, coffee waste is also easy to collect from the coffee shops, factory manufacturing coffee products and coffee cafes. Therefore, waste generated from coffee production can be used as a potential biowaste to synthesize adsorbents.

1.2 Problem Statement

Dye-containing effluents are increasing tremendously due to the ever-growing demand for the dyes in the industrial use and commercial purposes. The wastewater produced from these dye-utilizing industries mainly will result in the environmental pollution. One of the main reasons is because dyes contain ionic, cationic and aromatic organic compounds. These dyes tend to break down into smaller products that can be toxic, mutagenic and carcinogenic for human and all living organisms surrounding as well.

It is vital to remove all these kinds of hazardous pollutants from wastewater before it is disposed to the environmental water bodies. There are quite a few numbers of technologies have been applied worldwide to discharge dye-containing effluents namely, membrane separation, flocculation or coagulation, chemical oxidation and photocatalytic processes, electrochemical techniques, aerobic or anaerobic treatment and other methods. However, most of these approaches are very costly especially when large quantities of wastewater need to be treated. In view of this, adsorption has become one of the most versatile and efficient process due to its low-cost and flexibility in design and process operation. This is because no formation of
hazardous intermediates produced such as carbon dioxide and carbon monoxide gases from the adsorption method.

An effective and cheap alternative adsorbent is needed to remove dyes from wastewater in order to further reduce the cost of wastewater treatment. A wide range of biomass-based adsorbents have been tested to be efficient adsorbents for decolorizing dye wastewater. In this case, modified coffee ground was used as an efficient adsorbent to remove the dye-containing wastewater. This is due to its potential of colour removal from different classes of dyes with chemical modification. Hence, this study has unearthed the potential of modified coffee ground adsorbent to remove malachite green dyes from wastewater. As a consequence of high coffee production commercially, there is a larger amount of waste generation. Instead of disposing the coffee waste to the environment, it can be utilized by producing resourceful items that can give some advantages. In this project, my main aim is to remove malachite green dye using a bio-waste adsorbent which is coffee ground by modifying it with a chemical to enhance the adsorption efficiency.

1.3 Objectives

The objectives of this project are:

1) To prepare modified coffee ground adsorbent for the removal of malachite green dye using chemical activation.

2) To optimize the operating parameters for preparation of modified coffee ground adsorbent for the removal of malachite green dye.

3) To characterize modified coffee ground adsorbent in terms of surface area, surface morphology, elemental composition and surface chemistry.
4) To study the effect of adsorbate initial concentration, contact time, adsorbent dosage and solution pH for adsorption of malachite green for equilibrium and kinetic study.

1.4 Scope of Study

The scope of this study was mostly focusing on removal of malachite green using modified coffee ground. There are four objectives of this research project to be further investigated in this study. First of all, preparation and modification of coffee ground as a potential adsorbent to remove malachite green dye. Then, batch adsorption study for removal of malachite green dyes using coffee ground-based adsorbent were conducted. There were four parameters affecting rate of adsorption were used in this study such as solution pH, contact time, adsorbent dosage and initial dye concentration. Subsequently, the parameters were optimized using Response Surface Methodology (RSM) in order to get optimum condition for a higher adsorption capacity of MG dye. Finally, modified coffee ground adsorbent was characterized in order to study the surface area, surface morphology, elemental composition and surface chemistry.

1.5 Organization of Thesis

The research work consist of three chapters and the contents for each chapter in this study are as following:

Chapter 1: This chapter covers the background of this research which gives a brief introduction about water pollution, dye effluents waste from the industries, treatment of wastewater, removal of malachite green using coffee waste. This chapter also describes the problem statement, research objective and scope of the study.
**Chapter 2:** This chapter covers the literature review on water pollution from textile industry, technology for wastewater treatment, adsorbent and optimization using response surface methodology. Moreover, this chapter also explanations the factors affecting rate of adsorption and characterization of biomass-based adsorbent.

**Chapter 3:** This chapter covers the methodology used to conduct this study. It also comprises flow chart, materials, methods, optimization using Response Surface Methodology, batch adsorption study and characterization of adsorbent analysis to study on malachite green removal using coffee waste.