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FAKULTI BIOKEJURUTERAAN DAN TEKNOLOGI
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Spent Tea Grounds as A Cost-Effective Adsorbent for The Removal of Methylene Blue Dye

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J20A0587

A reported submitted in fulfilment of the requirements for the degree of Bachelor of Applied Science (Bioindustrial Technology) with Honours

FACULTY OF BIOENGINEERING AND TECHNOLOGY

UMK

2024

DECLARATION

I declare that this thesis entitled “Spent Tea Ground as A Cost-Effective Adsorbent for The Removal of Methylene Blue Dye” is the results of my own research except as cited in the references.

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Date : 10/3/2024

ACKNOWLEDGEMENT

First and foremost, I would like to thank University Malaysia Kelantan's Faculty of Bioengineering and Technology (FBKT) for allowing me to carry out this final year project as it gives me the exposure to the research field. It is my radiant sentiment to place on record my best regards to Dr. Mardawani Binti Mohamad, my supervisor, for all her aspiring guidance and for stimulating suggestions also giving invaluable constructive criticism and friendly advice. I choose this moment to acknowledge her contribution gratefully in helping me to coordinate my project, especially in writing this report. My sincere thanks to all the lecturers og Bioindustrial Technology (SBT) program and lab assistants for their careful and guidance which are extremely valuable for my study both theoretically and practically. I express my warm thanks to all my friends and family, especially to those who had helped throughout this entire process, without them I would not be able to complete my thesis. I am also using this opportunity to express my deepest gratitude to my parents Din Bin Ideris and Rahana Binti Jusoh for their support all this time, by keeping me harmonious and helping me put pieces together. Finally, it is a great pleasure to address people who helped me throughout this project to enhance my knowledge and laboratary skills, especially to Dr. Mardawani. May God bless you always.

Penyebatan Ampas Teh sebagai Penyerap Kos Efektif untuk Penyingkiran Pewarna Methylene Blue

ABSTRAK

Kebanyakan pewarna digunakan secara meluas dalam pencelupan industri yang berbeza tujuan seperti tekstil, makanan, kosmetik dan kertas percetakan. Antara contoh pewarna digunakan ialah Methylene biru (MB) yang paling biasa digunakan dalam pelbagai industri. Selain itu, Teh adalah salah satu yang paling banyak minuman popular dan kira-kira 3.5 juta tan teh telah dimakan setiap tahun di dunia (Kumar dan al., 2005). Tujuan kajian ini adalah untuk menggunakan Sisa Teh (TW) yang telah digunakan sebagai penyerap untuk penyingkiran MB. Berbeza-beza keadaan eksperimen diuji pada berbeza julat seperti kepekatan awal pewarna, dos bahan penjerap dan sentuhan masa. Dengan menggunakan sisa teh sebagai penjerap, ia menawarkan pendekatan yang mampan dan mesra alam untuk pengurusan sisa dan kitar semula. Ia membantu dalam mengurangkan jumlah sisa teh yang akan berakhir di tapak pelupusan sampah. Dengan sebatian sisa teh boleh mengikat secara berkesan dengan bahan pencemar, logam berat, pewarna, atau bahan cemar organik dalam air sisa, menyingkirkannya daripada air (Siam Hussain et al., 2018).

Kata kunci: Methylene Biru (MB), Sisa Teh (TW), Kepekatan awal pewarna, Dos bahan penjerap, Sentuhan masa.

Spent Tea Grounds as A Cost-Effective Adsorbent for The Removal of Methylene Blue Dye

ABSTRACT

Most dyes are widely used in various industrial dyeing purposes such as textiles, food, cosmetics, and printing paper. Among the examples of dyes used is Methylene Blue (MB) which is the most commonly used in various industries. Additionally, Tea is one of the most popular beverages, with approximately 3.5 million tons of tea consumed worldwide each year (Kumar et al., 2005). The purpose of this study is to use Spent Tea (TW) which has been used as an adsorbent for the removal of MB. Various experimental conditions were tested over different ranges such as initial dye concentration, adsorbent dosage, and contact time. By utilizing tea waste as an adsorbent, it offers a sustainable and eco-friendly approach for waste management and recycling. It helps in reducing the amount of tea waste that would otherwise end up in landfills. Tea waste's compounds can effectively bind with pollutants, heavy metals, dyes, or organic contaminants in wastewater, removing them from the water (Siam Hussain et al., 2018).

Keywords: Methylene Blue (MB), Tea Waste (TW), Initial dye concentration, Adsorbent dosage, Contact time.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Methylene blue (MB) is a commonly used dye in various industries, including textiles, printing, and pharmaceuticals. Its presence in wastewater streams can pose a significant environmental concern due to its toxic effects and potential to cause water pollution. Aside from having potential negative effects, the colour of the water caused by minute amounts of organic dyes is thought to be quite significant in industrial water pollution since it is also unsightly (Md. Tamez Uddin et al.,2008). Because of that, the colour water can have an impact on plant life, the tainting of water by various dyes has the potential to ruin an entire ecosystem. Some colours are even poisonous and cancer-causing. This demands that dye-containing water be treated before being disposed of in the environment (Md. Tamez Uddin et al.,2008).

Therefore, effective methods for the removal of methylene blue from wastewater are crucial to mitigate its adverse impact. Researchers have worked diligently to create activated carbon that is comparable to commercially available activated carbon in terms of cost, effectiveness, and environmental friendliness (M. Auta & B.H. Hameed, 2011). This has taken on a variety of forms, involving the use of different precursors such clays, polyethene, and agricultural waste-based materials, among others different preparation techniques and the use of different chemicals for activation (M. Auta & B.H. Hameed, 2011).

Adsorption has emerged as a promising technique for the removal of dyes from wastewater due to its simplicity, effectiveness, and cost-efficiency. Dyeing wastewater has been degraded using a variety of procedures up to this point, including coagulation, membrane filtering, photochemical degradation, chemical degradation, and biological degradation. These techniques have some effects on the degradation of dye wastewater, but they typically have a slow rate of degradation, large operational costs, and the potential to readily produce secondary pollutants.

The adsorption process is a simple, effective, and low-cost way to remove dyes (Hamidreza Sadegh et al., 2020). Activated carbon is widely recognized as a highly efficient adsorbent due to its large surface area, porous structure, and high adsorption capacity. Thus, using the chemical activation approach, the tea residue serves as an excellent precursor for the activated carbon with a promising adsorption capacity (J. Tao et al., 2019). However, the production of commercial activated carbon from conventional precursors can be costly and environmentally unsustainable (Jiazhen Zhou et al., 2018).

In recent years, there has been growing interest in exploring alternative and low-cost precursors for activated carbon production. Spent tea grounds, a byproduct of tea manufacturing and consumption, have gained attention as a potential precursor for activated carbon due to their abundant availability and rich carbon content (Jiazhen Zhou et al., 2018). By converting spent tea grounds into activated carbon, it is possible to transform a waste material into a value-added product while addressing the issue of disposal.

To optimize the adsorption performance of activated carbon derived from spent tea grounds, the use of Response Surface Methodology (RSM) offers a powerful tool. But in this study, the writer chooses Adsorption Equilibrium Method without using RSM. The adsorption equilibrium method is an approach used to measure the adsorption capacity of a particular adsorbent for a substance under equilibrium conditions. In this method, a solution containing the substance to be adsorbed (adsorbate) is prepared with various known concentrations. The adsorbent is then added to the solution and thoroughly mixed to reach equilibrium conditions.

Once equilibrium is reached, samples are taken from the solution and the remaining substance content in the solution (usually measured using chemical analysis techniques such as spectrophotometry) is measured. From this data, an adsorption equilibrium curve can be constructed, which depicts the relationship between the concentration of the remaining substance in the solution (or the amount of substance adsorbed) and the concentration of the substance in the liquid phase at equilibrium conditions.

Using data from the adsorption equilibrium curve, the maximum adsorption capacity of the adsorbent for a particular substance can be determined. Additionally, related parameters such as adsorption isotherms (such as Langmuir or Freundlich isotherms) can also be calculated to understand the adsorption behavior of the adsorbent in more detail.

The adsorption equilibrium method is commonly used in studies of adsorbent adsorption for various applications, including water treatment, gas purification, and adsorption in the pharmaceutical and chemical fields. This method provides valuable information about the adsorbent's ability to remove target substances from a solution under equilibrium conditions, which is crucial for designing and optimizing adsorption processes efficiently. While RSM is a statistical and mathematical approach that enables the simultaneous optimization of multiple variables by modelling the relationship between the independent variables and the response of interest. It allows for the identification of optimal process conditions that maximize the removal efficiency of methylene blue, leading to cost-effective and efficient adsorption systems.

Finally, in this investigation, STG were used for the removal of MB. The three parameters' variables were calculated: initial concentration, adsorbent dosage, and contact time, MB removal (%) and adsorption capacity (mg/g). Analytical and mathematical analysis methods were performed to examine the adsorption performance of STG for the removal of MB. Analysis of variance (ANOVA) was conducted to get significance model and applicability for MB removal (%) and adsorption capacity (mg/L).

1.2 Problem Statement

The presence of methylene blue (MB) dye in wastewater poses a significant environmental concern due to its potential toxicity and adverse effects on ecosystems. Effective and cost-efficient methods for the removal of methylene blue from wastewater are therefore crucial for environmental protection and water quality preservation. Conventional methods of dye removal, such as chemical precipitation or biological treatments, may be limited in terms of efficiency and cost-effectiveness. Activated carbon has proven to be a highly effective adsorbent for the removal of dyes from wastewater due to its high surface area, porous structure, and strong adsorption capacity. However, the production of commercial activated carbon from conventional precursors can be costly and may contribute to environmental degradation. Therefore, there is a need to explore alternative and sustainable precursors for activated carbon production that can provide comparable or improved adsorption performance at a lower cost.

Spent tea grounds, which are abundant byproducts of the tea manufacturing and consumption industry, offer a potential solution to this problem. By converting spent tea grounds into activated carbon, it is possible to transform a waste material into a valuable adsorbent while addressing the issue of waste disposal. However, there is a need to optimize the activation process of spent tea grounds to maximize the adsorption capacity of the resulting activated carbon for efficient methylene blue removal.

Therefore, the problem statement revolves around the need to develop an optimized and cost-effective adsorbent for methylene blue removal from wastewater using raw materials from spent tea grounds. The utilization of this experiment allows for the optimization of multiple variables, providing insights into the optimal conditions that maximize the adsorption efficiency and make the process economically viable. By addressing this problem, it becomes possible to develop a sustainable and efficient approach for dye removal in wastewater treatment.

1.3 Objectives

The objectives of this study were:

1. To evaluate the efficiency of raw materials spent tea ground as a cost-effective adsorbent on the removal of Methylene Blue (MB) from aqueous solution.

2. To investigate adsorption process parameters with (adsorbent dosage, contact time and initial concentration) on the removal of Methylene Blue (MB).

3. To study the interaction effect of process parameters on the percentage removal of Methylene Blue (MB).

1.4 Scope of Study

Biosorption experiments:

The biosorption studies were conducted by using desired quantities of the bioadsorbent (raw materials spent tea grounds) added to 100 mL of heavy metal solution in a 250 mL conical flask at room temperature. The samples were placed on the tabletop and left for 3 hours and taken at regular intervals. The adsorption experiments were carried out by varying initial concentration (mg/L), adsorbent dosage (g) and contact time (1-6 hours). The samples were filtered through filter paper and the concentration of the residue heavy metal solution was determined by using Ultraviolet-Visible Spectrophotometer. All the experiments were performed triplicate to assess reproducibility.

The second objective is to evaluate the performance of Spent Tea Grounds (STG) as an adsorbent for the removal of methylene blue from wastewater. This involves conducting adsorption experiments using STG under various conditions, such as different initial concentrations of methylene blue, adsorbent dosages, and contact times. The objective is to assess the adsorption capacity and efficiency of STG and understand the factors that influence the adsorption process.

To study the interaction effect of process parameters on the percentage removal of Methylene Blue (MB) with the test is conducted at initial concentration, doses of the adsorbent, and time intervals, therefore the removal efficiency must be computed. This formula is used to calculate the dye removal percentage.

$$\text{Removal Efficiency (\%)} = \frac{C0 - Cf}{C0} \times 100$$

Where, Ci and Cf is the concentration of MB initial and final respectively.

1.5 Significances of Study

The study addresses the environmental concern of methylene blue dye in wastewater. By developing a cost-effective adsorbent from a waste material like spent tea grounds, the study contributes to sustainable waste management practices and provides a potential solution for the removal of a harmful pollutant from water bodies. Undoubtedly, high content dye wastewater will lead to serious environmental issues such as colour pollution, light penetration interference, and virulence to aquatic organisms, even endanger human health (Hamidreza Sadegh et al., 2019).

By utilizing spent tea grounds as a precursor for activated carbon production, the study promotes the efficient use of renewable resources. It offers an alternative and sustainable approach to repurpose waste materials, reducing waste generation and minimizing the environmental footprint associated with conventional adsorbent production methods (Siam Hussain et al., 2018).

In addition, the study aims to develop a cost-effective adsorbent by utilizing low-cost and readily available spent tea grounds. This has the potential to reduce the overall cost of adsorption processes for methylene blue removal compared to commercially available activated carbon. It provides an economical solution that can be applied in wastewater treatment facilities or industries where cost efficiency is a priority.

The study aims to optimize the adsorption process. This allows for the identification of optimal process conditions that maximize methylene blue removal efficiency. The optimized conditions can lead to enhanced adsorption performance, reducing the amount of adsorbent required and improving the overall efficiency of the treatment process.

The study also contributes to the existing body of knowledge on the utilization of waste materials for activated carbon production and their application in wastewater treatment. It provides insights into the effectiveness of spent tea grounds as a precursor and the potential of adsorption equilibrium method for process optimization and the study's outcomes can have practical applications in industries and wastewater treatment

plants that deal with the removal of dyes or other organic contaminants. The optimized spent tea grounds can be implemented as an efficient and cost-effective adsorbent for methylene blue removal, potentially leading to improved water quality and reduced environmental impact.

Finally, the significance of the study lies in its potential to address environmental concerns, promote sustainable resource utilization, optimize the adsorption process, reduce costs, and contribute to the scientific understanding of using waste materials for adsorbent production and water treatment applications.

CHAPTER 2

LITERATURE REVIEW

2.1 Spent Tea Grounds (STG)

Tea waste, which refers to the leftover parts of tea leaves after brewing, such as tea bags or tea leaves, can be used in adsorption processes for various applications. Tea waste is abundantly available and often considered a waste product. Utilizing tea waste for adsorption provides a cost-effective alternative compared to synthetic adsorbents or commercially available activated carbon (Habib Dakhil, 2013).

By utilizing tea waste as an adsorbent, it offers a sustainable and eco-friendly approach for waste management and recycling. It helps in reducing the amount of tea waste that would otherwise end up in landfills. Tea waste contains compounds such as tannins, polyphenols, and other organic compounds that have the potential to adsorb various substances. These compounds can effectively bind with pollutants, heavy metals, dyes, or organic contaminants in wastewater, removing them from the water (Siam Hussain et al., 2018).

Tea waste also exhibits selectivity towards certain pollutants or compounds due to the presence of specific functional groups. This selectivity can be advantageous when targeting specific contaminants in wastewater treatment or other adsorption processes.

Tea waste can often be regenerated and reused as an adsorbent. After the adsorption process, tea waste can be treated or processed to recover the adsorbed substances or to restore its adsorption capacity for further use. This regeneration process contributes to the sustainability and cost-effectiveness of tea waste as an adsorbent. Lastly, it is important to note that the effectiveness of tea waste as an adsorbent can vary depending on factors such as the specific contaminants, pH conditions, contact time, and the composition of the tea waste itself. Experimental studies and optimization are typically required to determine the suitability and efficiency of tea waste for specific adsorption applications.

Overall, the many advancements in the use of wastes from the tea beverage industry for adsorption and the manufacturing of activated carbon, with an emphasis on the methodology used which are effectiveness of the removal process, properties of the material, and production techniques. The review shows that tea industry wastes provide a promising, affordable, and effective alternative adsorbent for removing different effluents from water (Siam Hussain et al., 2018).

In addition, caffeine in the leftovers may have a number of environmental consequences such as soil and water pollution. Furthermore, high biological oxygen demand (BOD) and chemical oxygen demand (COD) in tea production liquid effluent were detected (Okafor, 2021). Hence, before being released into the environment, the waste must be oxygenated, which the solid waste was often combusted or used as a natural fertilizer. The SEM picture of spent tea ground was shown in **Figure 2.1**.

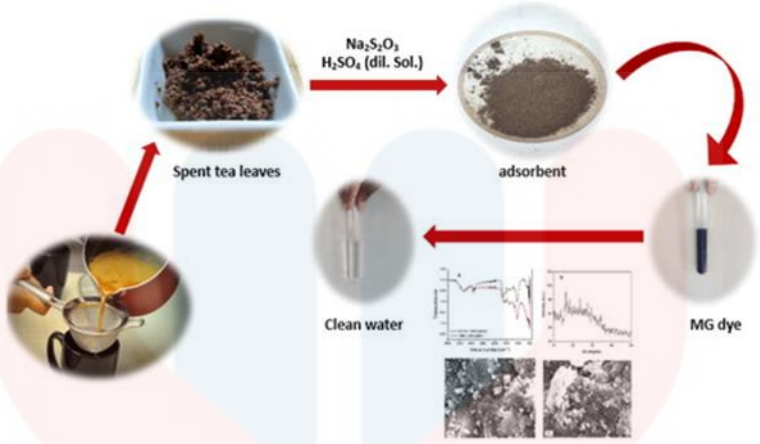


Figure 2.1: Images of Spent Tea Grounds and taken using a scanning electron microscope (SEM).

(Source: Priyanka Priyadarsini Samal et all., 2022)

2.2 Application to Spent Tea Grounds

Tea waste, when mixed with clay, can be used to create adsorptive membranes for removing toxic effluents generated as a byproduct in factories. This waste material, particularly black tea waste powder, has proven to be an effective adsorbent for dyes, which are commonly used in textiles, printing, papermaking, and cosmetics (Peter Keen., 2020). Approximately 2% of these dyes directly enter water resources, posing concentrated health hazards and serious toxicity. However, using oolong waste as an example, a study showed that it achieved an impressive 98% efficiency in removing methylene blue dye. In general, waste generated during the processing of any type of tea can be utilized for this purpose, offering a cost-effective alternative to more complex and expensive techniques like catalytic oxidation and membrane separation (Peter Keen).

Activated tea waste charcoal has also demonstrated its ability to adsorb lead, antibiotics, and heavy metals such as zinc, all at a lower cost. Activated carbon refers to carbon that has been processed to increase its surface area, allowing for greater adsorption capacity and stimulation of chemical reactions. The micro-porosity of activated carbon derived from tea waste enables a single gram of carbon to provide an extensive surface area of 30,000 square feet.

Traditionally, activated carbon has been produced from charcoal, which is a complex and relatively expensive process. However, biomass tea waste is emerging as a viable substitute. When lightly treated with sulfuric acid, it becomes a widely available and environmentally friendly resource. Furthermore, tea waste-based activated carbon offers additional properties that enable broader water purification, including the utilization of advanced technologies such as nanoparticles and capacitive deionization.

2.3 Biochar

The process of pyrolysis was employed to produce biochar, a substance abundant in carbon, from biomass (Tomczyk et al., 2020). In recent times, there has been a significant surge of interest in the topic due to its capacity to sequester carbon and enhance soil productivity. Biochar was a highly porous substance with a significant surface area that exhibited excellent adsorption properties for a diverse array of chemicals. (Premchand et al.,2023) discovered that the stability of the substance in soil was attributed to its high carbon content, which enabled it to persist for extended periods ranging from hundreds to thousands of years.

The utilization of biochar has been found by Zhang et al (2021) to possess the potential to enhance the physical properties of soil, such as its structure and water-holding capacity. This rendered it a significant soil amendment in a diverse range of agricultural and environmental contexts. According to Alkharabsheh et al. (2021), the utilization of biochar in agriculture had the potential to boost soil fertility and crop yields through various mechanisms such as augmenting water and nutrient retention, promoting microbial activity, and reducing soil erosion.

Castiglioni et al. (2022) suggest that biochar has the potential to serve as a filter medium in water treatment processes with the aim of removing various contaminants such as bacteria, heavy metals, and organic pollutants. Biochar exhibiting greater surface area demonstrated enhanced efficacy as an adsorbent for both cationic and anionic dyes. Hence, biochar has been deemed a viable and economical alternative to traditional silica and alumina adsorbents in the context of treating wastewater (Ullah et al., 2022).

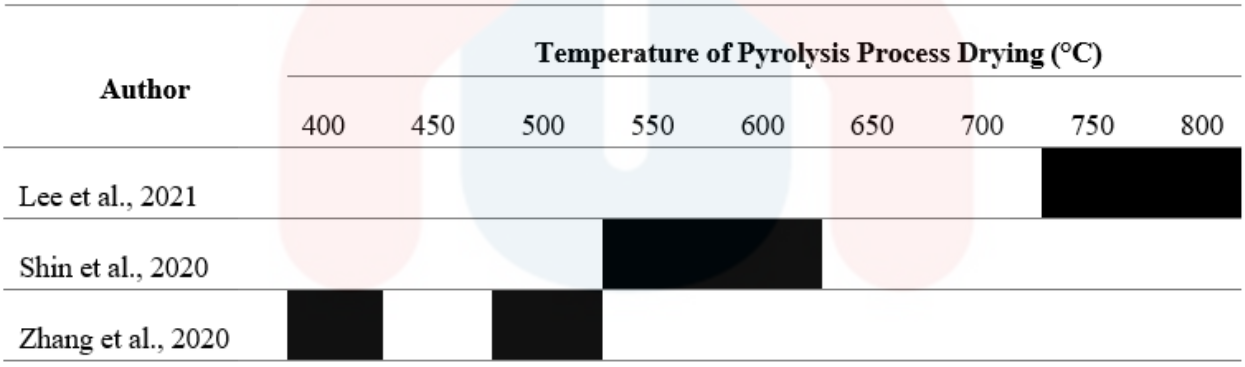
2.4 Pyrolysis Process

Pyrolysis was one of its most vital steps in creating biochar. In detail, great heat of temperature was used in an oxygen-free atmosphere. The process of producing Biochar from spent tea grounds involved the preparation of tea grounds that have been previously employed. Subsequently, the tea grounds undergone a drying process utilizing an oven set at a temperature range of 50-100°C, with a drying period that lasted between 12 and 24 hours (Nanang Ruhyat et al., 2022).

According to Amer & Elwardany (2020), an average temperature range of 400-800°C was typically employed during this process, with a pyrolysis duration spanning 1-2 hours. Additionally, the heating rate used was 100°C per minute. The pyrolysis process yields Biochar, which possesses chemical constituents including Sulphur (S), Carbon (C), Hydrogen (H), Nitrogen (N), Oxygen (O), as well as surface area and pore size. The utilization of Biochar as an alternative way of adsorbing environmentally harmful chemicals has been identified. **Table 2.1** presented the Temperature values obtained from various literature sources in the context of Biochar Pyrolysis Process.

Table 2.1: Use of Temperature in Biochar Pyrolysis Process Based on Literatures

(Source: Amer et al., 2019)



2.5 Biomass Carbonisation

Carbonisation is the process by which waste biomass is transformed into charcoal, a substance that is rich in carbon and energy (Chen et al., 2021). This redefinition pertains to the fundamental principles governing the utilization of renewable energy sources and the generation of power. Pyrolysis can be classified based on the rate of heating employed during the process, distinguishing between fast and slow pyrolysis (Al-Haj Ibrahim, 2020).

Fast pyrolysis is a thermal decomposition process characterized by a high heating rate and a relatively shorter residence time. In contrast, slow pyrolysis is characterized by reduced heating rates, leading to increased solid yields or char production. Therefore, our attention will be directed towards this process. Slow pyrolysis can be further categorized into two distinct processes: carbonization and torrefaction. Based on research made by Amer et al. (2019), the categorization is contingent upon the operational temperature of the procedure and the duration of time the substance remains within the system which were plotted in Table 2.2.

Table 2.2: A contrast between the processes of carbonization and torrefaction

	Carbonization	**Torrefaction**
Temperature (°C)	>300	200-300
Residence time	>2 hours and could reach days	< 2 hours
Fixed carbon (%)	85	30
Bio-oil yield (%)	30	5

The resulting substance from either of the two slow pyrolysis methods is commonly referred to as "char," whereas the term "charcoal" is specifically used for carbonization products. Charcoal is a carbonaceous substance primarily used as a fuel source. Charcoal can undergo additional processing to produce activated carbon, which serves as an adsorbent material. In addition, charcoal holds significant potential for utilization as a soil amendment, commonly referred to as "biochar" (Amalina et al., 2022).

2.6 Methylene Blue Dye

Figure 2.6.1: Methylene Blue

(Source: Civil Journal, 2018)

Methylene blue (MB) is a commonly used cationic dye in industries such as textiles, printing, and pharmaceuticals. Its presence in wastewater streams raises significant environmental concerns due to its toxic effects and potential for water pollution (Md. Tamez Uddin et al., 2008). The color of water contaminated with organic dyes, including methylene blue, not only affects the aesthetics but also has the potential to harm plant life and disrupt ecosystems. Some dyes are even known to be poisonous and carcinogenic (Md. Tamez Uddin et al., 2008). Consequently, it is essential to treat wastewater containing dyes before its disposal to mitigate these adverse impacts.

Researchers have focused on developing activated carbon as an effective and environmentally friendly method for dye removal. The goal is to create activated carbon that is comparable to commercially available options in terms of cost, effectiveness, and environmental sustainability. This has involved using different precursors, such as clays, polyethylene, and agricultural waste-based materials, as well as employing various preparation techniques and activation chemicals (M. Auta & B.H. Hameed, 2011). The chemical structure of Methylene Blue is depicted in **Figure 2.6.2**.

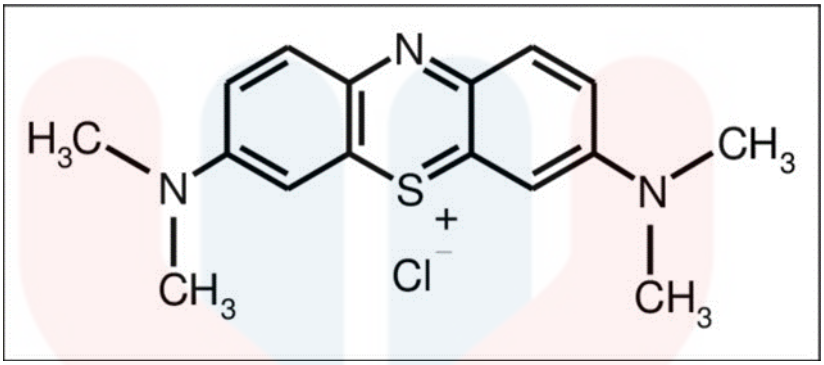


Figure 2.3: Molecular structure of Methylene Blue.

(Source: Civil Journal, 2018)

2.7 Application of Methylene Blue

Methylene blue (MB) has versatile applications in different fields. It is used in medicine as an antiseptic, antimalarial drug, diagnostic tool, and treatment for methemoglobinemia. In microbiology and laboratories, MB is employed as a staining agent and indicator dye. In the textile industry, it serves as a dye for fabrics. Additionally, MB is used in research and scientific studies for various experiments. It is important to use MB under proper guidance to ensure safety and efficacy in specific applications.

2.8 Adsorption Technique

2.8.1 Definition of Mechanism

Adsorption is a phenomenon characterized by the accumulation of one substance onto the surface of another substance within a solution. The commencement of adsorption primarily arises from the presence of unstable forces within the solution or on the surface of solid materials. In a broad sense, absorption was described as the process by which a substance uniformly distributed throughout a larger volume. The sorption process was recognized as a simultaneous occurrence of both adsorption and absorption processes (Gupta, 2023).

The adsorption system comprises both the adsorbent and the adsorbate, which were both integral components of the solution. Adsorbents possess the inherent propensity to attract adsorbates present in the bulk solution. The adsorption efficacy was contingent upon various factors, encompassing surface charge, contact time, concentration of the dye, temperature, the existence of functional groups, and the pH level (Vojnović et al., 2022). The process of adsorption depicted in **Figure 2.8.**

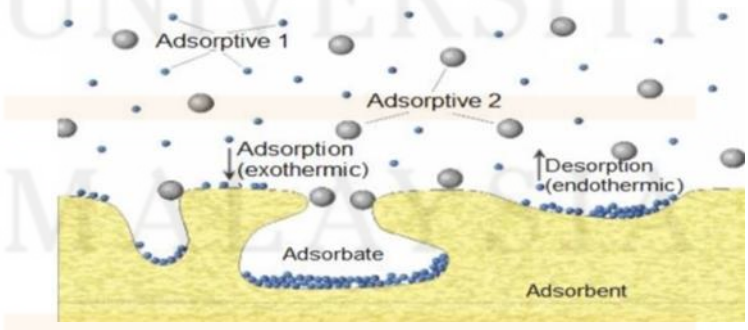


Figure 2.8: Mechanism of Adsorption Process.

(Source: The Engineering Concepts, 2021)

2.8.2 Type of Adsorption Process

There are two main types of adsorptions: physisorption and chemisorption. Physisorption occurs when the molecules of an adsorbate are weakly bound to the surface of an adsorbent through forces like Van der Waals interactions (Soliman & Moustafa, 2020). For example, the deposition of ammonia gas onto activated charcoal demonstrates physisorption. On the other hand, chemisorption involves the adsorbate being attracted to the adsorbent surface through chemical forces and forming chemical bonds (Gil, 2023). An example of chemisorption is the deposition of oxygen on tungsten surfaces. When it comes to the removal of Malachite Green by spent coffee grounds biochar, both physisorption and chemisorption mechanisms are likely involved. Initially, physisorption plays a significant role, followed by potential chemisorption as the dye interacts with functional groups on the bio-char surface.

Table 2.8 presented a summary of the distinguishing characteristics of physisorption and chemisorption processes.

Chemisorption	Physisorption
Attracted by a chemical bond force	Dominated by Van der Waal's forces
Process is irreversible	Process is reversible
The procedure requires activation energy.	There is no requirement for activation energy.
At high temperatures, this is advantageous.	Preferably at a low temperature.

Table 2.8: The properties of both the physisorption and chemisorption processes.

(Source: Agboola & Benson, 2021)

2.9 Central Composite Design (CCD)

Central Composite Design (CCD) was used to fit a quadratic surface and aid in the optimization of the useful parameters with the least amount of experimentation (Bhattacharya, 2021). The Central Composite Design (CCD) was a design that incorporated two levels, namely full factorial or fractional factorial. It included additional center points and axial points, also referred to as star points, as depicted in **Figure 2.5**. The center point was positioned at the central location, while the axial points were situated at the midpoint of the factor levels for each level of the other factors. Hence, the coordinates for the axial points were (-1, 0), (1, 0), (0, -1), and (0, 1).

In the shown design in **Figure 2.5 (b)**, the axial (star) points are positioned on the surface of the square box within the 2^2 designs. Hence, the design illustrated in **Figure 2.5 (b)** can be regarded as a 3^2-factorial design, allowing for the application of a complete quadratic model (second-order regression) to fit the response surface. The inclusion of multiple center points allows for the examination of lack-of-fit as well. The distance between the center and the axial points is represented by the symbol α. In this design shown in Figure 2.5 (b), α was equal to 1.

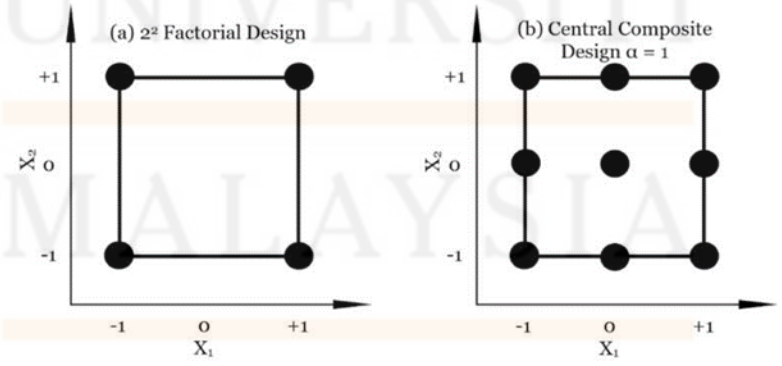


Figure 2.9: Central Composite Design, CCD (right) from the 2^2 Factorial Design (left) (Source: *The Open Educator - 2. Design Response Surface Methodology*, 2022)

The placement of axial points on the circle in a 22-factorial design, specifically at the corner points, provides additional advantages, including improved rotatability of the design. The enhanced rotatability of the design enables accurate prediction of outcomes within the defined range of independent variables, also referred to as x-variables or predictor variables in the context of response surface methodology (RSM) and regression analysis.

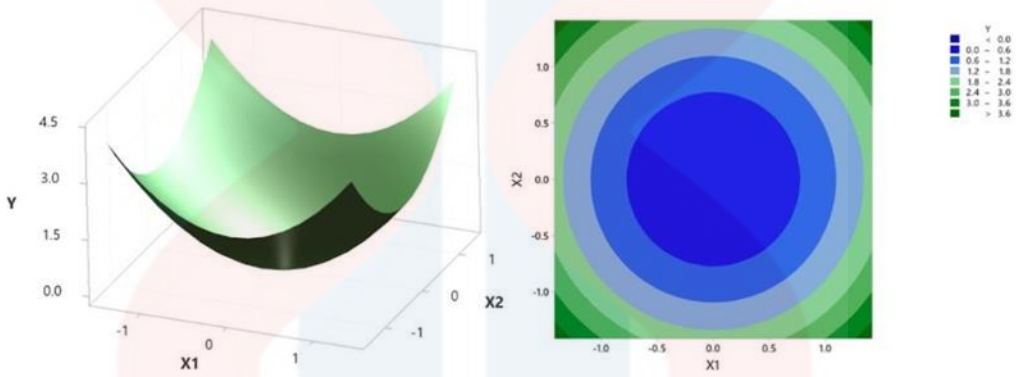


Figure 2.9: Central Composite Design, CCD with Consistent and Stable Variance.
(Source: *The Open Educator - 2. Design Response Surface Methodology*, 2022)

A prediction model is considered robust when it consistently and stably generates variability across all independent or predictor variables. Figure 2.6 showcased a prediction model with favorable attributes, such as consistent and stable variances across the entire range of independent variables. For the optimization study in this research, Design Expert Software version 13.0 was utilized.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The raw materials used in this study are spent tea grounds that will be collected at Restaurant Nasi Ayam Kukus Jeli, Kelantan, and distilled water. Approximately, 2.46 kg of the spent tea grounds were washed with tap water and distilled water several times to remove all the dirt particles till the washing water contains no color.

3.2 Apparatus

The apparatus used in this research were reagent bottle (100 mL and 1000 mL), beaker (100 mL and 1000 mL), filter funnel, measuring cylinder (5 mL, 10 mL and 50 mL), conical flask (250 mL), cuvette (2 cm path length), filter paper, glass rod, and spatula.

3.3 Equipment

For this research, the equipment's were used a oven, UV-Vis Spectrophotometer (Genesys 20), and analytical balance (SARTORIUS). The software used for the mathematical analysis optimization study was Excel.

3.4 Chemical

The chemicals that were utilized in this research were Methylene Blue (MB) dye powder, and distilled water.

3.5 Preparation The Raw Material of Spent Tea Grounds

The absorbent utilized in this study was obtained by collecting tea waste from households. Tea waste refers to the leftover tea dust after consumption. The collected material underwent multiple rinses with both tap water and distilled water to eliminate any dirt particles. Subsequently, it was boiled with distilled water to eliminate caffeine, tannin, and other dyes, and washed repeatedly with distilled water until the washing water was colorless. The rinsed material was then dried at a temperature of 70 ◦C for a duration of 24 hours. After drying, the raw material was crushed, and stored in plastic sample for applications.

3.6 Preparation of Methylene Blue Dye Stock Solution

To prepare the stock solution, 1000 mg/L of MB (with a dye content of 1g) was be dissolved in 1 L of impurified distilled water. The test solutions were then prepared by diluting the stock solution to the desired concentrations. The estimation of adsorption capacities relied on the proportion of pure dye material present in the final product.

3.7 Preparation of MB Calibration Curve

The MB dye stock solution was diluted to concentrations of 0.5, 2, 4, 6, 8, and 10 mg/L using Equation (3.1). A blank sample of distilled water was utilized. The blank and the dye solution were introduced into the UV-spectrophotometer at a wavelength of 661 µm, and subsequently, the absorbance readings were recorded. The absorbance measurement of the MB dye solution was performed in triplicate, and the resulting values were averaged. The collected data was used for the purpose of constructing a standard calibration curve. The final concentration of MB dye after the adsorption process was determined using the standard calibration curve.

$$M_1V_1=M_2V_2 \quad \text{……. Equation (3.1)}$$

Where M_1 is an initial molarity, V_1 is an initial volume, M_2 is the final molarity, V_2 is the final volume.

3.8 Batch Adsorption Studies

Batch adsorption studies were carried out using the spent tea grounds as an adsorbent. The constant parameters in this study were time (3 hours), adsorbent size (using the raw material size), temperature (37°C), and volume of MB dye solution (1000mL). On the other hand, the three manipulated variables were contact time, adsorbent dosage, and initial concentration of MB dye. The contact time was varied from 1 hour to 6 hours. For adsorbent dosage, the range was 0.5g, 1.0g, 1.5g, 2.0g, 2.5g, and 3.0g. The range of initial MB dye concentration was 20 mg/L to 100 mg/L.

In this experimental design, the percentage of MB dye removal (%) and adsorption capacity (qe), were the response as shown in **Table 3.8.1, 3.8.2, 3.8.3**. A total of 10 experimental runs were generated. Each experimental was conducted triplicate to obtain more accurate results. After 3 hours, a sample was filtered from the conical flask, and the solution was analyzed for residual dye concentration. The concentration of MB was determined spectrophotometrically by monitoring the absorbance at 661 µm.

The percentage for dye removal was calculated using Equation (3.2) while Equation (3.3) was utilized to calculate the adsorption capacity of the adsorbent.

$$\text{Percentage of MG removal (\%)} = \frac{C0 - Cf}{C0} \times 100 \qquad \text{Equation 3.1}$$

Where C0 is the initial concentration and Cf is the final concentration of MB solution.

While the adsorption capacity will be measured using Equation 3.2:

$$\text{Adsorption capacity (mg/g), qe} = \frac{C0 - Cf \times V}{} \qquad \text{Equation 3.2}$$

Where, Co represents initial concentration and Cf represents final concentration of the MB solution. V is the volume of MB solution in L, and m is the mass of adsorbent in grams.

Initial concentration(mg/mL)	R1	R2	R3	Average	SD	RSD (%)
20	0.183	0.183	0.183	0.183	0.000	0.0000
30	0.283	0.282	0.281	0.282	0.001	0.3546
40	0.366	0.365	0.365	0.365	0.001	0.2740
50	0.486	0.488	0.488	0.487	0.001	0.2053
60	0.481	0.479	0.479	0.480	0.001	0.2083
70	0.626	0.625	0.625	0.625	0.001	0.1600
80	0.600	0.599	0.599	0.599	0.001	0.1669
90	0.685	0.684	0.686	0.685	0.001	0.1460
100	0.639	0.640	0.640	0.640	0.001	0.1563

Table 3.8.1: Experimental design matrix of initial concentration using Excel.

Adsorbent dosage (g)	R1	R2	R3	average	SD	RSD (%)
0.5	0.196	0.196	0.196	0.196	0.000	0.000
1.0	0.234	0.235	0.235	0.235	0.001	0.246
1.5	0.196	0.195	0.196	0.196	0.001	0.295
2.0	0.154	0.154	0.154	0.154	0.000	0.000
2.5	0.169	0.169	0.169	0.169	0.000	0.000
3.0	0.167	0.167	0.166	0.167	0.001	0.346

Table 3.8.2: Experimental design matrix of adsorbent dosage using Excel.

Time (h)	R1	R2	R3	average	SD	RSD (%)
1.0	0.182	0.182	0.182	0.182	0.000	0.000
2.0	0.224	0.223	0.223	0.223	0.001	0.259
3.0	0.228	0.228	0.226	0.227	0.001	0.508
4.0	0.230	0.229	0.229	0.229	0.001	0.252
5.0	0.209	0.208	0.208	0.208	0.001	0.277
6.0	0.223	0.223	0.222	0.223	0.001	0.259

Table 3.8.3: Experimental design matrix of contact time using Excel.

3.8.1 Effect of Initial Dye Concentration

The experiments were conducted in 250 mL conical flask, agitating at 3 hours and 37°C with varies of working solution which were 10,20,30,40,50,60,70,80,90 and 100 mg/L prepared by diluting the MB dye stock solution into desired concentration. Afterwards, the working solution was filtered using filter paper and being placed into cuvette which was then will be inserted into UV-spectrophotometer at wavelength 661 µm to obtain absorbance readings. The result was recorded.

3.8.2 Effect of Adsorbent Dosage

The prepared solutions, which consisted of adsorbent dosages of 0.5 g, 1.0g, 1.5g, 2.0g, 2.5g, and 3.0g, along with 100 mL of concentration 100mg/L, were agitated at 3 hours and 37°C until the desired adsorbent dosage was reached. Afterward, the solutions were filtered using filter paper and transferred to a cuvette. The cuvette was then inserted into a UV-spectrophotometer set to a wavelength of 661 µm to measure the absorbance reading. The result was recorded.

3.8.3 Effect of Contact Time

The study investigated the impact of varying contact durations, specifically 1h, 2h, 3h, 4h, 5h, and 6h, on the removal of MB dye. The experiment involved agitation of a conical flask at a temperature of 37°C. The determination of MB dye concentration after the adsorption process involved the filtration of the solution through filter paper, followed by the measurement of adsorbance readings using a UV-spectrophotometer at a wavelength of 661 µm. The result was recorded.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Results

MB Concentration (mg/L)	Average Absorbence Reading (g)
0.5	0.323
2	0.493
4	0.784
6	0.815
8	1.272
10	1.470

Table 4.1: The Average Absorbance Readings of different MB Concentration

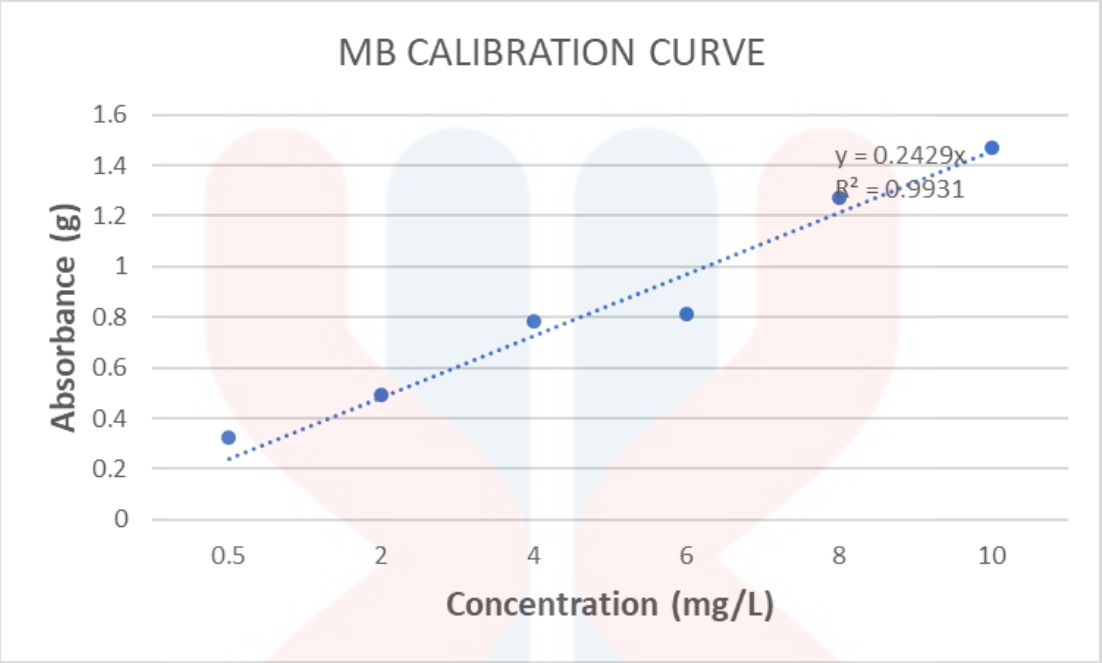


Figure 4.1: Calibration Curve for Methelyne Blue (MB) Dye

4.2 Discussion

A calibration curve is a graphical representive of the relationship between the concentration of a substance in a sample and the response of an analytical instrument, such as a spectrophotometer. In the context of spectroscopy, it typically relates the absorbance or intensity of light to the concentration of a substance in a solution. To construct a calibration curve, known standard solutions with varying concentrations of the substance are analyzed using the instrument, and their corresponding responses such as absorbance values are recorded like shows in Table 4.1 the average absorbance readings of different MB concentration (mg/L).

This curve serves as a reference to determine the concentration of the substance in MB samples in different solutions by measuring their response and comparing it to the curve. Calibration curves also are essential in quantitative analysis, providing a means to accurately determine the concentration of a substance in a sample based on instrumental measurements.

In this experiment, analysis of methylene blue in different solutions was conducted. The results for before and after adsorption are very important for the adsorption study. The UV-vis spectrophotometric method was used to analyze the methylene blue in different solutions. One of the most widely used analytical methods is UV-Vis spectrophotometry, which utilizes ultraviolet and visible light to measure the absorbance of a chemical compound in a sample. Where the absorbance value of the light that is passed will be proportional to the concentration of the solution in the cuvette.

A calibration curve was constructed by plotting the absorbance as a function of respective concentrations of methylene blue in solution at 0.5, 2, 4, 6, 8, and 10 mg/L. The straight line of the absorbance vs. concentration of methylene blue passing through the origin in Figure 4.1 suggested the validity of Beer-Lambert law. The concentration of MB in different solutions was determined from measurement of absorbance divided by the slope of the calibration curve.

In figure 4.1 shows the calibration curve for Methelyne Blue (MB) Dye. Based on the figure, the relationship between the absorbance reading and the MB concentration was almost into linear relationship. When the relationship of the calibration was linear, the slope was a degree of sensitivity. Based on these data, a linear regression equation Y = 0.2429x is obtained with a correlation coefficient (R) of 0.9965 and a coefficient of determination (R2) of 0.9931 so that the linearity of the standard solution with a range of 0.5-10 mg/L is more than 99%.

A correlation coefficient of 1 indicates a perfect linear relationship, while a correlation coefficient of 0 indicates no linear relationship. A correlation coefficient of at least 0.95 is generally considered to be acceptable for most analytical methods. By having a correlation coefficient ≥ 0.99, the calibration curve meets the requirements of linearity acceptance so that the test results on the standard solution used are proportional to the concentration of analytes in the sample.

4.2.1 Effect of Initial Dye Concentration

Initial concentration(mg/mL)	R1	R2	R3	Average	SD	RSD (%)
20	0.183	0.183	0.183	0.183	0.000	0.0000
30	0.283	0.282	0.281	0.282	0.001	0.3546
40	0.366	0.365	0.365	0.365	0.001	0.2740
50	0.486	0.488	0.488	0.487	0.001	0.2053
60	0.481	0.479	0.479	0.480	0.001	0.2083
70	0.626	0.625	0.625	0.625	0.001	0.1600
80	0.600	0.599	0.599	0.599	0.001	0.1669
90	0.685	0.684	0.686	0.685	0.001	0.1460
100	0.639	0.640	0.640	0.640	0.001	0.1563

Initial concentration(mg/mL)	R1	R2	R3	Average	SD	RSD (%)
20	0.183	0.183	0.183	0.183	0.000	0.0000
30	0.283	0.282	0.281	0.282	0.001	0.3546
40	0.366	0.365	0.365	0.365	0.001	0.2740
50	0.486	0.488	0.488	0.487	0.001	0.2053
60	0.481	0.479	0.479	0.480	0.001	0.2083
70	0.626	0.625	0.625	0.625	0.001	0.1600
80	0.600	0.599	0.599	0.599	0.001	0.1669
90	0.685	0.684	0.686	0.685	0.001	0.1460
100	0.639	0.640	0.640	0.640	0.001	0.1563

Table 4.2.1 Initial of Dye Concentration (mg/L)

Initial concentration (mg/mL)	Final concentration (mg/mL)	Percentage removal of MB (%)
20	1.1610	94.20
30	1.5040	94.99
40	2.0063	94.98
50	1.9747	96.05
60	2.5744	95.71
70	2.4674	96.48
80	2.8201	96.47
90	2.6335	97.07
100	0.0000	100.00

Table 4.2.2 Percentage Removal of MB for Initial Concentration

The effect of initial concentration refers to how variations in the initial concentration of a substance to be adsorbed affect the adsorption process. In the context of using spent tea grounds as an adsorbent for the removal of methylene blue dye, the influence of the initial concentration of methylene blue in the solution on the removal efficiency can be closely observed.

The effect of initial dye concentration on the adsorption of MB was conducted at a different concentration of MB ranging from 20 mg/L to 100 mg/L shown in table 4.2.1. The adsorbent dose 1g were added to 100 ml MB solution with a room temperature (25±2) ℃ for 3 hours. The colour change of the solution after 3 hours can be observed in the image in the appendix section.

Impact on adsorption capacity depends on the higher the initial concentration of a substance to be adsorbed, the more of that substance is available to interact with the adsorbent. This can increase the adsorption capacity, which is the maximum amount of substance that can be adsorbed by adsorbent under certain conditions. This can be seen in table 4.2, the higher of initial concentration 100 mg/L has the higher the percentage removal of MB which is 100%. While the lower of initial concentration is 20 mg/L has the lowest of the percentage of MB which is 94.20%. Generally, the higher the initial concentration of the substance to be adsorbed, the higher the removal efficiency, especially in the initial stages of the adsorption process.

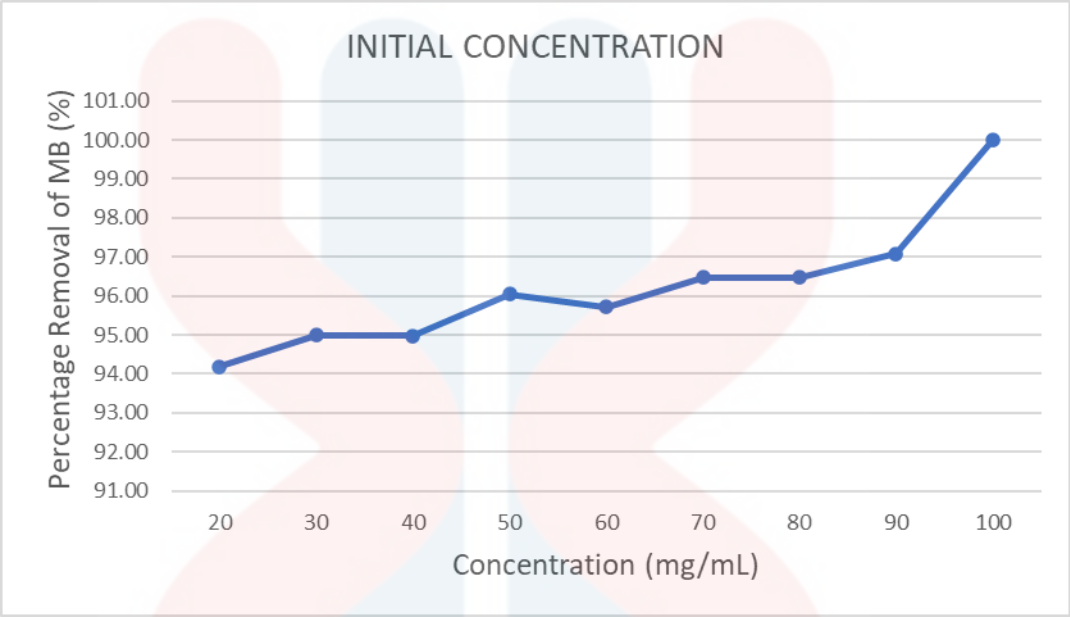


Figure 4.2: Concentration vs Removal Efficiency (%) of MB at Different Concentration Solution.

In Figure 4.2 shows that the percentage removal (96.05%) for initial concentration at 50 mg/L was decreased into (95.71%) of percentage removal for initial concentration at 60 mg/L. This is because of changes in adsorption rate. Initially, with increase of initial concentrations, the adsorption rate to be faster in early because there are more molecules of the susbstance availabe to be adsorbed by the adsorbent. However, in over time of process, the adsorption rate may slow down as the adsorption capacity of the adsorbent approaches saturation and a certain limit when the adsorption capacity of the adsorption is reached.

4.3 Effect of Adsorbent Dosage

Adsorbent dosage (g)	R1	R2	R3	average	SD	RSD (%)
0.5	0.196	0.196	0.196	0.196	0.000	0.000
1.0	0.234	0.235	0.235	0.235	0.001	0.246
1.5	0.196	0.195	0.196	0.196	0.001	0.295
2.0	0.154	0.154	0.154	0.154	0.000	0.000
2.5	0.169	0.169	0.169	0.169	0.000	0.000
3.0	0.167	0.167	0.166	0.167	0.001	0.346

Table 4.3: Concentration of Dye Solutions at Different Adsorbent Dosage.

Adsorbent dosage (g)	Final Concentration (mg/mL)	Percentage Removal Of MB (%)
0.5	0.807	99.193
1.0	0.966	99.034
1.5	0.806	99.194
2.0	0.634	99.366
2.5	0.696	99.304
3.0	0.686	99.314

Table 4.3: Percentage Removal of MB for Adsorbent Dosage Effect

In this study, the effect of adsorbent dosage was recorded into table 4.3 and 4.3. Generally, increasing the dosage of adsorbent will lead to a higher adsorption capacity. One important factor is the dosage of the adsorbent, which determines its capacity for a particular initial concentration of the adsorbate under operating conditions (Amode et all., 2016). Thus, adsorbent dose is an important factor that affects the adsorption performance. The influence of adsorbent dose in adsorption of MB was studied to obtain a most appropriate amount of adsorbent at the same of MB concentrations. The effect of adsorbent dose was studied by 100 mg/L of 10 ml MB concentrations under different adsorbent doses (0.5 g, 1.0 g, 1.5 g, 2.0 g, 2.5 g and 3.0 g), as shown in table 4.3 above. A similar trend in adsorption behavior of MB concentrations with different adsorbent dose was observed after 3 hours. The result in image form was obtained in appendix section.

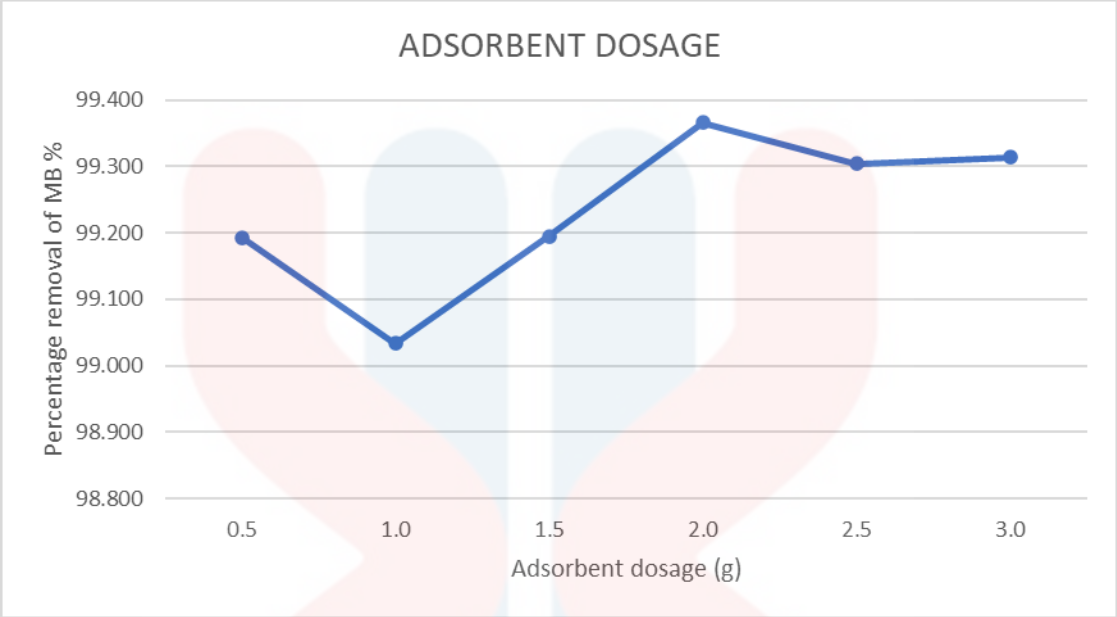


Figure 4.3: Adsorbent vs Removal Efficiency (%) of MB at Different Adsorbent Doses.

The effect of adsorbent dosages on removal of MB dye solution has been presented in Figure 4.3. The experiments were carried out by varying the biosorbent dosages from (0.5g, 1.0g, 1.5g, 2.0g, 2.5g, and 3.0g). The sorption capacity of biosorbent increases with increasing the adsorbent dosages. This is due to the availability of more functional groups and surface area at higher dosages. It was observed that the highest removal efficiency of 99.37% adsorption at an adsorbent dosage of 2.0g but at a lower dosage of 0.5g a removal efficiency of 99.19% is achieved. This is because a greater amount of adsorbent provides more surface area and available binding sites for the adsorbate molecules to adhere to, resulting in greater removal of the target susbtance from the solution.

On further increasing the adsorbent dose to 3.0 g, an increasing trend in removal efficiency was observed from 0.5g to 1.0g and continued to increase to 2.0g. The removal efficiency from 2.0g decreased to 2.5g and increased slightly to 3.0g. This is because of diminishing returns which is while increasing the adsorbent dosage initially leads to a proportional increase in adsorption capacity, there may be a point of diminishing returns. This means that at a certain dosage level, further increases in adsorbent amount may not result in significant improvements in adsorption capacity. This is because the availability

of binding sites on the adsorbent may become saturated or reach their maximum capacity. In the case of MB concentration maximum removal was attained at 2.0g of adsorbent weight.

4.4 Effect of Contact Time

Time (h)	R1	R2	R3	average	SD	RSD (%)
1.0	0.182	0.182	0.182	0.182	0.000	0.000
2.0	0.224	0.223	0.223	0.223	0.001	0.259
3.0	0.228	0.228	0.226	0.227	0.001	0.508
4.0	0.230	0.229	0.229	0.229	0.001	0.252
5.0	0.209	0.208	0.208	0.208	0.001	0.277
6.0	0.223	0.223	0.222	0.223	0.001	0.259

Table 4.4: Concentration of solution at different time intake.

Time (h)	Final Concentration (mg/mL)	Percentage Removal Of MB (%)
1.0	0.749	99.251
2.0	0.919	99.081
3.0	0.936	99.064
4.0	0.944	99.056
5.0	0.858	99.142
6.0	0.917	99.083

Table 4.4: Percentage Removal of MB for Contact Time Effect

The effect of contact time refers to how the duration of contact time between the adsorbent and the solution affects the adsorption process. In the context of adsorption, it describes how quickly or slowly the adsorbent can adsorb the target substances from the solution under certain conditions. The tables above show that the effect of contact time on the removal of dye was studied in different time duration. Table 4.4 shows the concentration of MB after treating with the adsorbent at the time ranging from 1.0 to 6.0 hours. At this experiment, even the time is different but the dosage adsorbent still same which is 2g.

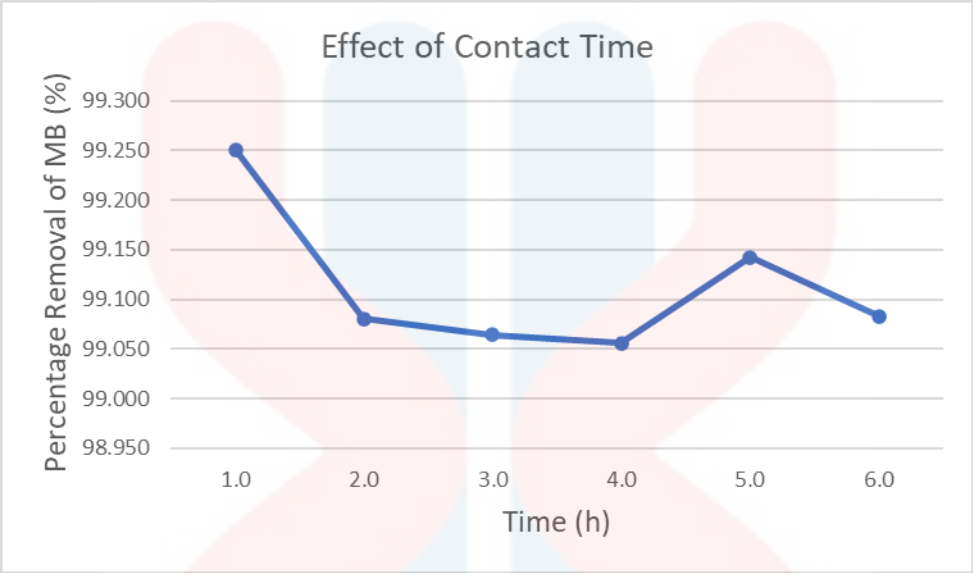


Figure 4.4: Adsorbent vs Removal Efficiency (%) of MB at Different Time.

The effect of equilibration time it is possible that the adsorption process reaches equilibrium or near-equilibrium conditions within the first hour. After this point, additional contact time may not significantly increase the adsorption capacity or efficiency of the adsorbent, leading to diminishing returns in terms of percentage removal.

Hence, the adsorption sites on the adsorbent material may become saturated with methylene blue molecules after 1 hour, especially if the initial concentration of MB is relatively high. Once the adsorption sites are fully occupied, the contact time may not result in additional adsorption, leading to a plateau or decrease in percentage of removal.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In conclusion, Spent Tea Grounds (STG) offer a cost-effective alternative as an adsorbent for methylene blue removal compared to conventonal adsorbents. Their availability as a waste product from tea processing industries makes them environmentally friendly and economically viable for wastewater treatment applications. Hence, the effectiveness of STG is demonstrated through batch adsorption experiments, with significant percentages of MB removed from aqueous solutions. Thus, the study revealed that the highest percentage of removal of methylene blue occurred after 1 hour of contact time is sufficient to achieve efficient adsorption.

5.2 Recommendations

There are several recommendations can be considered to enhance the effiency of the removal of MB dye from the aqueous solution using spent tea grounds. Firstly, conduct further study to optimize adsorption parameters such as pH and temperature to achieve adsorption capacity and efficiency of STG for methylene blue removal. Thus, for the future study, there are several suggestions can be made in order to gain a better performance for the experimental work. One of the suggestions is by performing the adsorption process using other agriculture wastes to prevent the accumulation of plant biomass.

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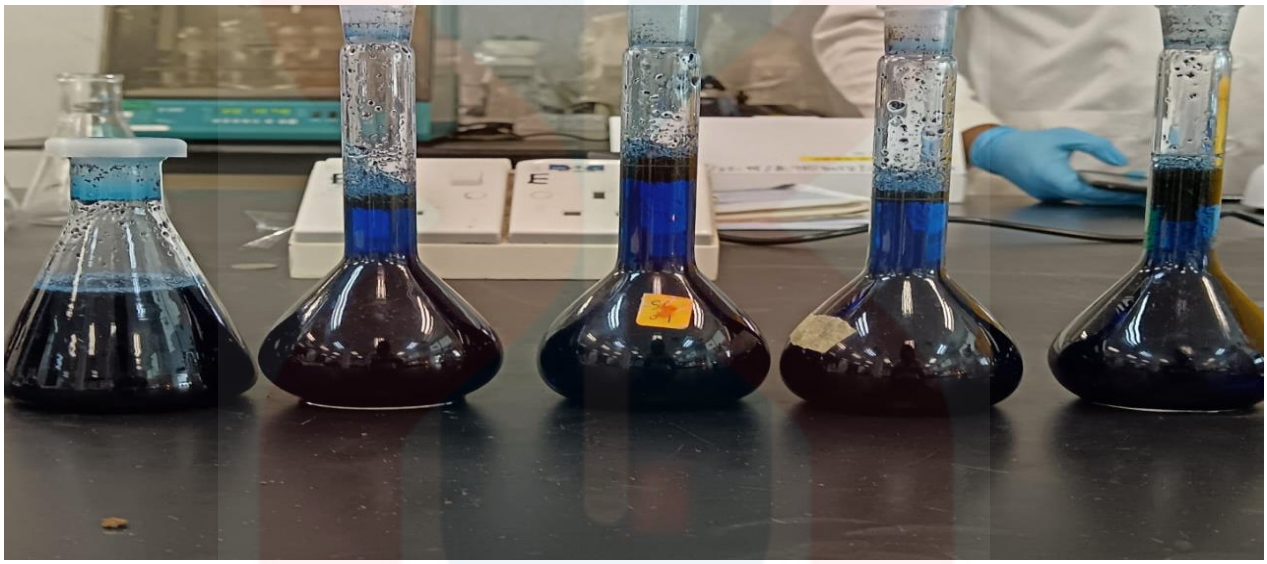
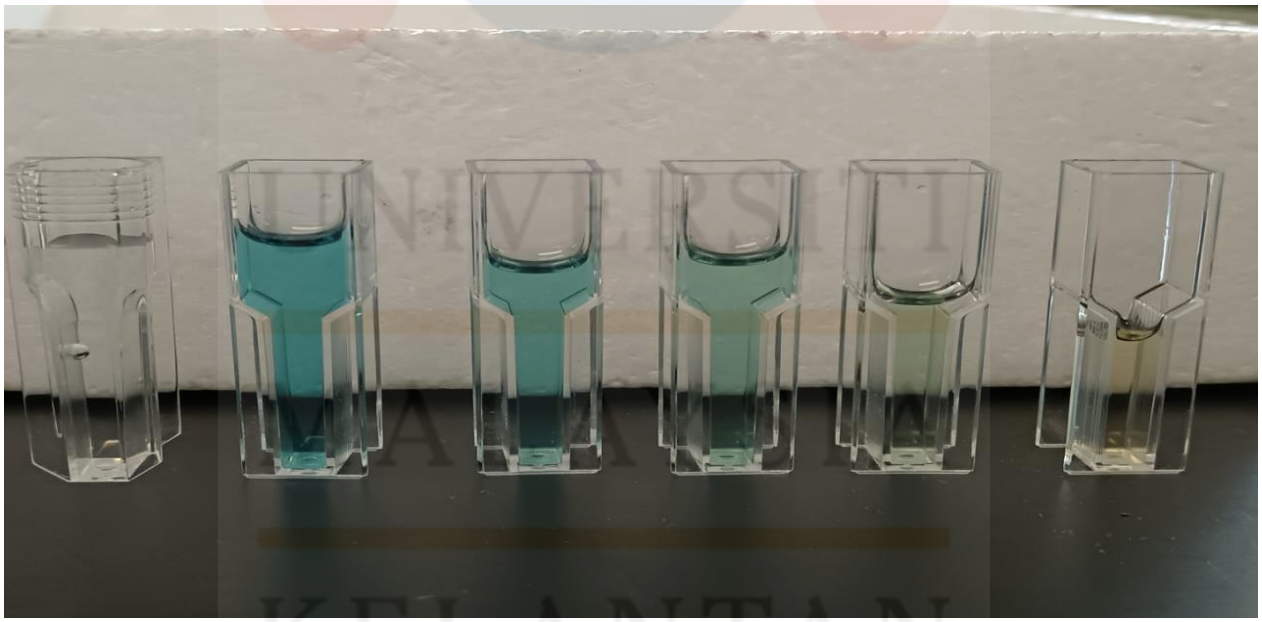
APPENDIX A

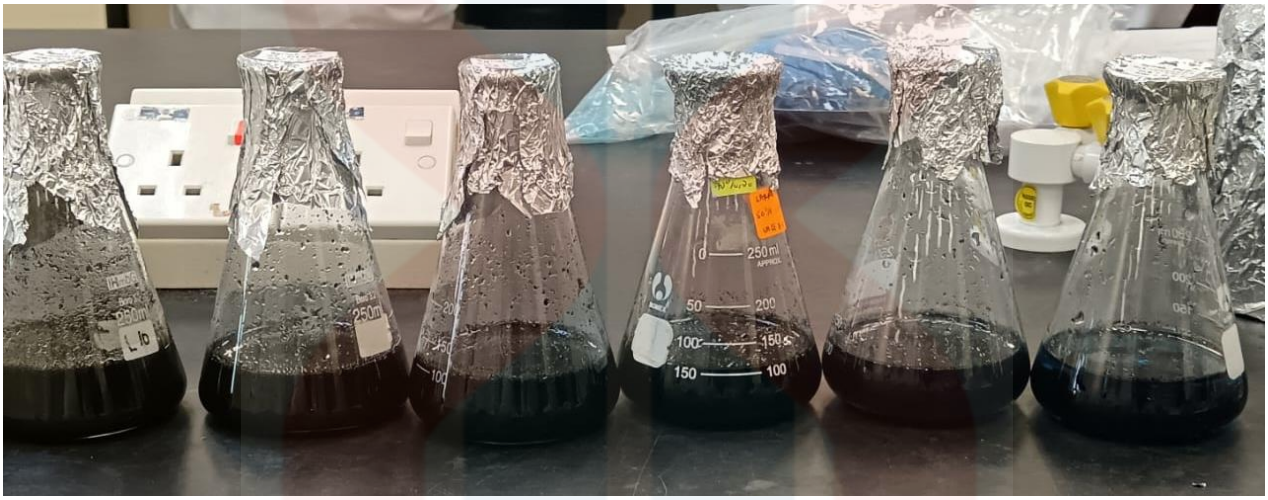
1) Effect of parameter initial concentration (before and after adsorption process):

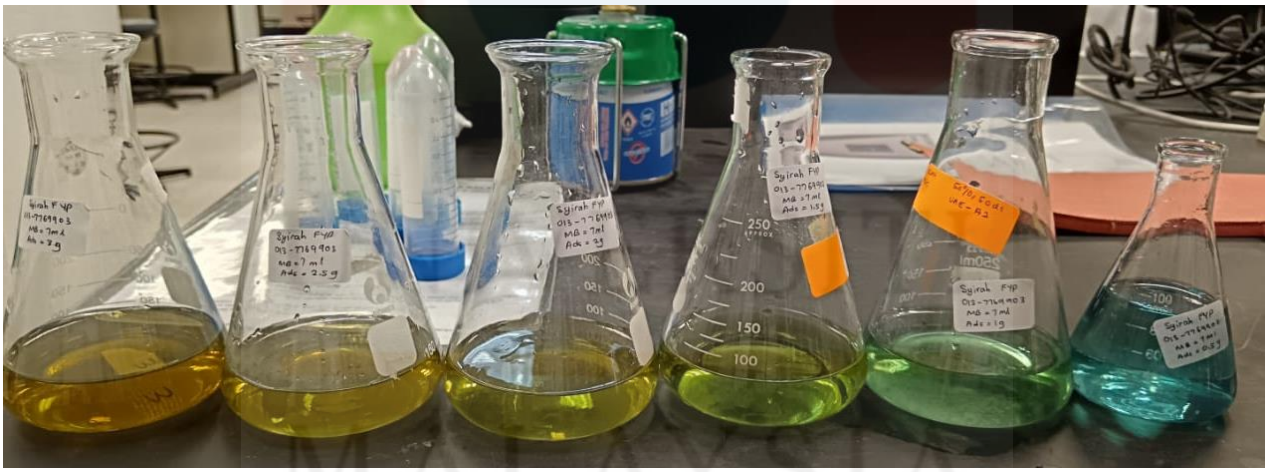




APPENDIX B

2) Effect of adsorbent dosage (before and after adsorption process):





APPENDIX C

3) Effect of parameter contact time (before and after adsorption process):