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Utilizing Biochar Derived from *Garcinia Mangostana* peel as an Adsorbent for Removing Congo Red Dye from Aqueous Solutions

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DECLARATION

I declare that this thesis entitled Utilizing Biochar Derived from Garcinia Mangostana peel as an Adsorbent for Removing Congo Red Dye from Aqueous Solutions is the result of my research except as cited in the references.

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Stamp : ____________________________

Date : ____________________________

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PENGGUNAAN BIO-ARANG YANG DIPEROLEH DARIPADA KULIT MANGGIS SEBAGAI PENYERAP UNTUK MENYINGKIRKAN PEWARNA MERAH CONGO DARI LARUTAN AKUEUS

ABSTRAK

Kajian ini mengkaji potensi bio-arang yang diperoleh daripada kulit 'Garcinia' manggis sebagai penjerap untuk penyingkiran pewarna Merah Congo daripada larutan akueus. Bahan mentah yang digunakan dalam kajian ini dikumpulkan daripada sisa pertanian dari ladang pisang dalam kg. Kuala Lipis, kawasan Pahang. Kulit manggis adalah salah satu sisa pertanian yang sering dilihat sebagai berharga di pasaran selepas musim menuai pokok manggis. Sisa pertanian adalah istilah untuk sisa bahan dari pertanian. Kulit manggis adalah sisa pertanian yang murah dan mampan yang boleh digunakan untuk menyingkiran air sisa logam berat dan pewarna. Hari ini, majoriti proses penjerapan digunakan untuk merawat air tercemar dari pelbagai industri, seperti tekstil, penyamakan kulit, lilin, farmaseutikal, dan lain-lain, menggunakan sisa pertanian. Cara yang paling berkesan untuk menghapuskan bahan pencemar, logam berat, dan pewarna dari air sisa adalah penjerapan. Kos - penjerap berkesan yang boleh menyingkirkan pewarna dari larutan akueus adalah kulit manggis. Matlamat utama kajian ini adalah untuk mengetahui sejauh mana kulit manggis mentah menyingkirkan pewarna Congo Merah dan keupayaannya sebagai penjerap. Dengan penggunaan analisis FT-IR, sifat kulit manggis telah dikaji. Untuk mencari parameter yang ideal dan isoterma penjerapan untuk penyingkiran pewarna merah kongo menggunakan kulit manggis, parameter ini telah di. Peratusan maksimum penyingkiran pewarna diperhatikan dalam 1.5 g selepas jam 8 pada 700˚C suhu pengkarbonan dan 30 mg/L kepekatan pewarna awal. Isoterma Langmuir menyediakan yang paling sesuai untuk data keseimbangan, dan kecekapan penjerapan adalah 85.47 mg/Tingkah laku penjerapan telah dianalisis menggunakan model Langmuir mempamerkan tahap kesesuaian yang tinggi ($R^2 = 0.9998$) untuk penjerapan pewarna Merah Congo pada bio-arang, menunjukkan penjerapan monolayer pada permukaan homogen.

Kata kunci: Penjerapan, Sisa pertanian, Penjerap, Larutan berair, dan Isoterma Langmuir

Utilizing Biochar Derived from *Garcinia Mangostana* peel as an Adsorbent for Removing Congo Red Dye from Aqueous Solutions

ABSTRACT

This study investigates the potential of biochar derived from Garcinia mangostana peel as an adsorbent for the removal of Congo Red dye from aqueous solutions. The raw material that was used in this study was collected from agricultural waste from the banana farm in kg. Kuala Lipis, Pahang area. The mangosteen peel is one of the agricultural wastes that is often seen as valuable in the market after the harvesting season of the mangosteen tree. Agricultural waste is the term for leftover materials from agriculture. Mangosteen peel is an inexpensive and sustainable agricultural waste that can be used to rid wastewater of heavy metals and dyes. These days, the majority of the adsorption process used to treat polluted water from various industries, such as textile, tannery, candle, pharmaceutical, etc., uses agricultural wastes. The most efficient way for eliminating pollutants, heavy metals, and dyes from wastewater is adsorption. A cost - effective adsorbent that can remove dye from an aqueous solution is mangosteen peel. This study's primary goal is to find out how well raw mangosteen peel absorbs dye Congo Red and its capabilities as an adsorbent. With the use of FT-IR analysis, the properties of mangosteen peel were investigated. In order to find the ideal parameters and adsorption isotherms for the removal of congo red dye using mangosteen peel, these parameters were examined. The maximum percentage of dye removal was observed in 1.5 g after 8 hours at 700˚C of carbonization temperature and 30 mg/L of the initial dye concentration. The Langmuir isotherm provided the best fit for the equilibrium data, and the adsorption efficiency was 85.47 mg/g. The adsorption behavior was analyzed using the Langmuir model exhibited a high degree of fit ($R^2 = 0.9998$) for the adsorption of Congo Red dye on biochar, indicating monolayer adsorption on a homogeneous surface.

Keywords: Adsorption, Agricultural waste, Adsorbent, Aqueous solution, and Langmuir Isotherm

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

%	Percentage
Q_E	Equilibrium concentration of dyes on the adsorbent (mg/g)
K_l	Langmuir Constant (L/mg)
K_F	Constant value which related to adsorption capacity (mg/g)
mg/L	Miligram per litre
g/L	Gram per Litre
mL	Mililitre
mm	Milimitre
˚C	Degree Celsius
h	Hour
nm	Nanometer
C_o	Initial Concentration of adsorbent
C_e	Final Concentration of adsorbent
UV	Ultraviolet
FTIR	Fourier Transforms Infrared Spectroscopy
L	Liter
g	Gram
kg	Kilogram
XRF	X-ray Fluorescence
µL	Microlitre

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Garcinia Mangostana, popularly known as "Mangosteen," is a tropical fruit native to Southeast Asia. Its peel has been widely studied for its potential use as an adsorbent in wastewater treatment. This paper uses Mangosteen peel as an adsorbent for removing Congo Red dye from aqueous solutions. Hence, Congo Red is a synthetic azo dye extensively used in the textile industry (El-Shafey E.I, J. Hazard. Mater., 2010). The dye removal has a complex molecular structure. Unfortunately, it poses a severe environmental hazard as it is toxic and carcinogenic to living organisms, including humans. Thus, cost-effective and eco-friendly technology is needed to remove this dye from wastewater before being discharged into the environment (Sharma et al., 2014).

Adsorption is a widely studied and promising alternative for removing Congo Red dye. The technique involves the interaction of adsorbate Congo Red with the adsorbent (Mangosteen peel). One of the factors affecting adsorption efficiency is the surface area of the adsorbent. Mangosteen peel's surface area is between 4.26 to 133.3 m^2/g, making it an excellent candidate for Congo Red adsorption. Several previous studies have investigated the use of Mangosteen peel for removing dyes and other contaminants from aqueous solutions. One survey by (Tan et al. 2012) showed that the adsorption kinetic of Congo Red onto Mangosteen peel followed the pseudo-second-order model. Their findings indicated that Mangosteen peel is a promising biosorbent for Congo Red removal. Another study by Wu et al. (2020) investigated the combined use of Mangosteen peel and Chitosan for Congo

Red adsorption. The results showed a significant improvement in removing Congo Red, with approximately 94% of the dye extracted at optimal conditions. The researchers concluded combining Mangosteen peel, and Chitosan could be a practical and cost-effective solution for treating Congo Red wastewater.

To summarise, Mangosteen peel offers a promising alternative for removing Congo Red dye from aqueous solutions. Its high surface area and potential for adsorption make it a viable and eco-friendly option for wastewater treatment. Future research should analyze the optimal conditions for adsorption, including carbonization temperature, and initial dye concentration.

1.2 PROBLEM STATEMENT

The main contributors to water pollution are the textile industry which is due to the release of various hazardous dyes. Congo red is one of the most used dyes in this industry and has been linked to several adverse effects on human health and the environment. Therefore, finding an effective and eco-friendly way to remove this dye from wastewater is paramount. Garcinia mangostana peel, a waste product of the fruit processing industry, has shown promising results as an adsorbent for Congo red dye removal. It contains high levels of natural compounds with strong adsorption capacity and can effectively remove pollutants from aqueous solutions. This method is cost-effective, readily available, and sustainable, making it an ideal solution for industrial dye removal.

The main problem this study aims to address is the need for a reliable and effective method to remove Congo red dye from wastewater. Using Garcinia mangostana peel as an adsorb, we can address this problem and use a waste product that would otherwise have been discarded. In conclusion, the use of Garcinia mangostana peel as an adsorbent for the removal of Congo red dye has the potential to be a sustainable and effective solution for water pollution caused by the textile industry. Further research and implementation of this method can contribute to a cleaner and safer environment.

1.3 OBJECTIVES

1. To investigate the effectiveness of biochar from Garcinia Mangostana peel in removing Congo red dye from aqueous solutions.

2. To determine the experimental parameters for removing Congo red dye using biochar from Garcinia Mangostana peel, such as initial carbonization temperture, initial dye concentration, contact time, absorbent, and dosage.

3. To characterize Garcinia Mangostana peel as an adsorbent using Fourier-transform infrared spectroscopy (FTIR).

1.4 SCOPE OF STUDY

This uses the mangosteen peel used as an adsorbent to remove the Congo red dye in an aqueous solution. The removal of Congo Red dye from industrial wastewater has been a growing concern due to its carcinogenicity. One potential solution is the use of Garcinia mangostana peel, which has been shown to have a high adsorption capacity for various pollutants. The purpose of this research is to examine the efficiency of G. mangostana peel in removing Congo Red dye from industrial wastewater using FTIR analysis.

FTIR analysis will identify the functional groups on the surface responsible for the adsorption of Congo Red dye. The data collected from these analyses will better understand the adsorption mechanism and the optimal conditions for maximum dye removal. This study has the potential to not only lessen the adverse effects of Congo Red dye on the environment but also utilize an otherwise unused waste product, G. mangostana peel, as a practical adsorbate analysis and experimentation could lead to a more sustainable and cost-effective approach to industrial wastewater treatment.

1.5 SIGNIFICANT OF THE STUDY

The release of dyes into aqueous solutions has been a significant environmental problem due to their toxicological effects and persistent nature. The use of biochar has recently gained attention as a potential adsorbent for the removal of pollutants from water sources. Using biochar derived from Garcinia Mangostana peel as an adsorbent for removing Congo Red dye from aqueous solutions has been a topic of recent research.

showed how that biochar derived from Garcinia Mangostana peel was an effective adsorbent for Congo Red dye removal from aqueous solutions. The biochar showed a high adsorption capacity due to its mesoporous structure and high surface area, allowing maximum contact with the dye molecules. It was also found that the efficiency of the adsorption process increased with an increase in the biochar dosaUsinge of biochar in water remediation has proven to be a cost-effective and eco-friendly method for removing pollutants from water sources. The utilization of Garcinia Mangostana peel-derived biochar as an adsorbent for Congo Red dye removal shows excellent potential in water treatment. In conclusion, using biochar derived from Garcinia Mangostana peel as an adsorbent for Congo Red dye removal has been a promising water treatment method. Further studies are required to explore the full potential of biochar as an adsorbent for various pollutants in aqueous solutions.

CHAPTER 2

LITERATURE REVIEW

2.1 ADSORPTION

Adsorption is a process in which molecules of a substance, called an adsorbate, accumulate on the surface of solid material, called the adsorbent. This process is commonly used in various fields, including water treatment, gas purification, and separation of substances. Adsorption can be classified into two main types: chemical and physical. Also attributed to as physisorption, physical adsorption occurs when the adsorbate is held on the surface of the adsorbent by weak Vander Waals forces (chu et al., 2023). In contrast, chemical adsorption, too known as chemisorption, involves the chemical growth bonds from adsorbent to adsorbent. surfaces.

Thus, adsorption procession depends on the surface area, temperature, pressure, and adsorbate concentration. The surface area of the adsorbent plays a crucial role as it provides a larger size for the contact of the adsorbate molecules. As temperature rises, there is an increase in the rate of adsorption due to the expanded dynamic vitality of the adsorbate molecules. Similarly, increased pressure enhances the adsorption, resulting in a higher concentration of adsorbate molecules. Adsorption is used in a diverse range of applications. In water treatment, adsorption removes pollutants like heavy metals, dyes, and pesticides from water. Activated carbon is regularly utilized as an adsorbent in water treatment processes. In gas purification, adsorption removes impurities like carbon dioxide, sulphur dioxide, and nitrogen from the gas stream. Zeolites and activated alumina are commonly used as adsorbents in these processes. To sum up, adsorption plays a crucial role in various fields, including gas purification, water treatment, and separation of substances. Understanding the underlying principles of physical and chemical adsorption is essential for effectively designing and optimizing adsorption processes.

2.1.1 FACTOR AFFECTING THE ADSORPTION

Adsorption is a process that involves the adhesion of molecules or particles on a solid surface or interface, forming a layer called the adsorbate. The adsorption process is widely used in wastewater treatment, gas purification, and catalyst industries. Several factors can affect the adsorption state, including surface area, pore size, the chemical composition of the adsorbent, pH, temperature, and contact time. Based on the previous studies (as listed in Table 2.1), there has been proven that Surface area is one of the essential factors affecting the adsorption state. It influences the number of surface sites accessible for adsorption. A larger surface area of the adsorbent would mean more active sites for adsorption, resulting in higher adsorption capacity. For instance, activated carbon has a high surface area due to its micro-porous structure. Activated carbon efficiently removes methylene blue dye from wastewater, with a percentage ranging from 79.37% to 99.4% depending on the contact time and initial dye concentration Table 2.1 (Yagub et al., 2014).

Table 2.1: The Effect of contact time on the percentage of dye removal

Adsorbents	**Dye name**	**Contact time range**	**Percentage of removal range (%)**	**References**
Activated Carbon	Methylene Blue	30-90 min	79.37%-99.4%	(Yagub et al.,2014)
Nanosize Porous carbon	Crystal Violet	30 min	96.69%	(Ho et al., 2013)

Thus, the Pore size is another factor that affects the adsorption state. It determines the size of the molecule adsorbed, as pores of a specific size can only accommodate molecules of a similar size. For example, Nanosized porous carbon has a pore size of approximately 10 nm. It efficiently removes crystal violet dye from wastewater, with a removal percentage of 96.69% at an adsorbent dose of 0.05 g/L and a contact time of 30 min, as Table 2.1 shows above (Ho et al., 2013).

Table 2.2: The Effect of adsorbent dosage on the percentage of dye removal

Adsorbents	**Dye name**	**Adsorbents dosage range** (g/L or mg/L)	**Percentage of removal range (%)**	**References**
Pineapple peel powder	Methylene Blue	0.5 and 1.5 g/L	46.5%-97.54%	(M et al., 2011)
Chitosan	Malachite green	5 and 20 mg/L	94%-99%	(Liang et al., 2014)

Table 2.2 above shows the amount of adsorbent used and the dosage affecting adsorption efficiency. The optimal dosage range can vary for different adsorbates and adsorbents. For instance, in the adsorption of Methylene Blue (MB) dye onto Pineapple Peel Powder (PPP), the optimal dosage range was between 0.5 and 1.5 g/L. While for Malachite Green (MG) dye adsorption onto Chitosan, the optimal dosage range was between 5 and 20 mg/L. The percentage of removal, or the percentage of adsorbate removed from the aqueous solution, is another crucial factor determining adsorption efficacy. The removal range rate depends on the adsorbent and adsorbate under consideration. For the adsorption of MB dye onto PPP, the removal percentage was found to be between 46.5% to 97.54%, while for MG dye adsorption onto Chitosan, it was 94% to 99%.

Table 2.3: The Effect of pH on the percentage of dye removal

Adsorbents	Dye name	pH	Percentage of removal range (%)	References
Activated carbon	Congo Red	4-10	80%	(R Cho S, 2016)
Zeolite	Cationic and Anionic	4-8	92%	(S Kan S, 2012)

Table 2.3 above shows the impact of pH on the dye removal percentage. One type of adsorbent is activated carbon, and the other is zeolite. Activated carbon is a versatile adsorbent that effectively removes organic and inorganic pollutants like dyes from wastewater. For instance, the activated carbon can remove Congo red with a percentage removal of 80% in the pH range of 4-10. Meanwhile, zeolite is a highly porous material that can remove cationic and anionic dyes. Alizarin blue was successfully removed from the aqueous solution with a percentage removal of 92% in the pH range of 4-8. The ability of the adsorbents to adsorb can be strongly impacted by the pH of the solution. The adsorbent can have maximum adsorption capacity at a specific pH range along with the of development of complex species between the adsorbate and the adsorbent. However, the adsorption capacity can decrease sharply at values above or below this pH range. Therefore, pH optimization is a crucial step in the adsorption process.

Additionally, activated carbon is an adsorbent with a more extraordinary ability to eliminate colors seeing as its higher surface area and mesoporous structure. Another type of adsorbent, graphene oxide, contains numerous functional groups and a substantial surface area that increase its binding affinity for dyes, as Table 2.4 shows below.

Table 2.4: The Effect of Initial Dye Concentration on the Percentage of dye Removal

Adsorbents	Dye name	Initial dye Concentration (g/L or mg/L)	Percentage of removal range (%)	References
Activated carbon	Methylene Blue	50 mg/L	90-98	(V K Su, 2009)
Graphene Oxide	Reactive Blue	25 mg/L	94-99	(Zhang S Xu., 2019)

It is significant to remember that the initial dye concentration and the type of adsorbent employed affect the percentage of removal range. The adsorption mechanism involves various processes, such as physical adsorption, chemisorption, and electrostatic interaction. Thus, optimizing the conditions for adsorption would result in better efficiency. Overall, the adsorption process is an affordable and eco-friendly way to remove dyes from effluent, and using biochar as an adsorbent shows excellent promise for wastewater treatment.

2.1.2 ADSORPTION ISOTHERM

Adsorption isotherm is a phenomenon where molecules or particles are attracted to and accumulate within the solid or liquid's surface. In biochar, adsorption isotherm refers to the correlation among the concentration of a particular substance in solution and the amount of that substance adsorbed onto the biochar surface. By studying adsorption isotherms, we can understand how biochar behaves as a sorbent for different contaminants, essential for evaluating its potential in environmental applications.

2.1.3 LANGMUIR ADSORPTION ISOTHERM MODEL

The most common type of adsorption isotherm used in biochar research is the Langmuir isotherm, which assumes monolayer adsorption and constant adsorption energy for all sites. The Langmuir isotherm is expressed as q = max (KC)/(1+KC), where q is the amount of substance adsorbed per unit mass of biochar, max is the maximum adsorption capacity, K is the adsorption constant, C is the concentration of a substance in solution. The Langmuir isotherm can be used to estimate the total amount of meaning that can be removed by a given amount of biochar and to compare the adsorption capacity of different biochar samples.

2.1.4 FREUNDLICH ADSORPTION ISOTHERM MODEL

Another commonly used adsorption isotherm is the Freundlich isotherm, which assumes multilayer adsorption and a heterogeneous adsorption energy distribution. The Freundlich isotherm is expressed as q = KF(C)n, where KF and n are the empirical constants that characterize the adsorption intensity and capacity, correspondingly. It can utilize the Freundlich isotherm to estimate the potential adsorption capacity of biochar for a wide range of contaminants and to compare the adsorption performance of different biochar samples.

To sum up, studying adsorption isotherms is a crucial aspect of biochar research, as it provides insights into the resistance and adsorption capacity of biochar for various pollutants. Adsorption can be predicted using two popular models: Langmuir and Freundlich's isotherms capacity and the comparison of biochar samples. Further research in this area could lead to using biochar as an effective and sustainable solution for environmental contamination.

2.2 DYE

Dye classification is the process of categorizing dyes based on specific properties or characteristics. One way to categorize dyes is based on their origin, resulting in two main categories: natural and synthetic dyes removal.

Natural dyes have been used for centuries before synthetic dyes were invented. They are derived from plant, animal or mineral sources. Extracting natural dyes is labour-intensive and dependent on seasonality and geography. Some of the most commonly used natural dyes include indigo, derived from the leaves of the indigo plant; madder, derived from the roots of the madder plant; and cochineal, derived from a tiny insect found on cacti. Natural dyes are known for their rich and unique hues but are often less vibrant and less colourfast than synthetic dyes.

On the other hand, synthetic dyes are chemically produced and usually offer more consistent and vibrant colours. They were first discovered in the mid-19th century and rapidly replaced natural dyes. One of the earliest synthetic dyes was mauveine, discovered by William Henry Perkin in 1856. Since then, the production of synthetic dyes has increased significantly, and they are now used in the vast majority of textile, paper and plastic products. However, there are concerns about synthetic dyes' environmental impact and ways to mitigate them. Figure 2.2 below shows the classification of dye removal was summarized.

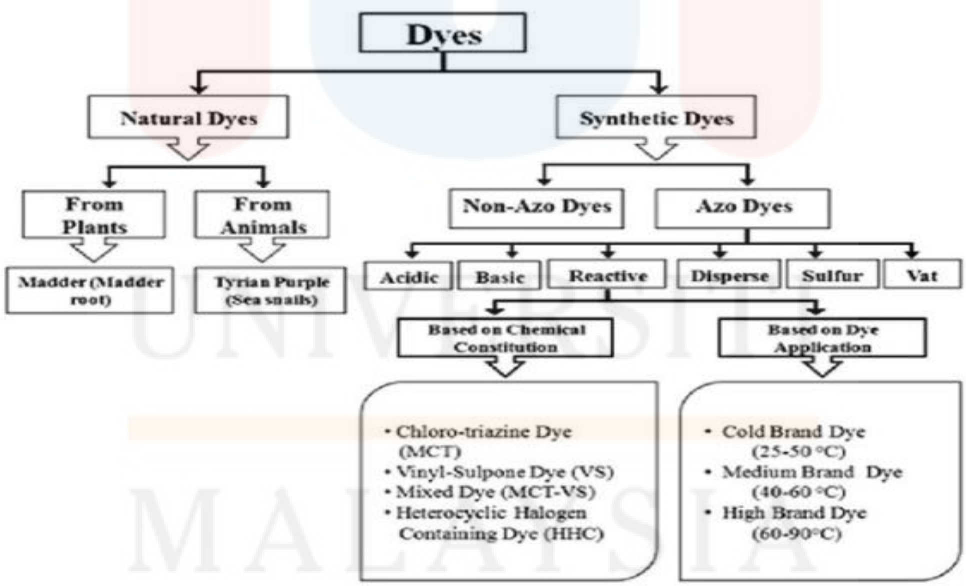


Figure 2.1: The Classification of dyes (Ahmet et al., 2016)

As Figure 2.1 shows above, synthetic dyes are further divided into subcategories based on their chemical structure and properties. For example, acid dyes are used for colouring protein fibres like wool and silk, while basic dyes are used for synthetic fibres like polyester. Meanwhile, dispersed dyes are used in the colouring of synthetic fibres, whereas reactive dyes are used for cellulosic fibres such as cotton. Classifying dyes into natural and artificial categories provides helpful information about their origin, production process, and properties. While natural dyes offer unique colours but may be less consistent and less colourfast, synthetic dyes offer vibrant and consistent colours but are also associated with environmental concerns. Nevertheless, understanding the classification of dyes can help decision-makers in the industry to make informed decisions about the types of dyes removal to use in production.

2.3 SYNTHETIC DYE

Synthetic dyes have been widely used in various industries due to their ability to impart colour to multiple substrates. These dyes are classified based on their chemical structure and the principal substrate they are used on. Thus, there are a few chemical categories of synthetic dyes, including acid, reactive, dispersed, direct, primary, and vat dyes (Singh et al., 2017). Each type has a unique mechanism for applying colour to its principal substrate. For instance, acid dyes are used to colour wool, silk, and nylon, as they are water-soluble and acidic. Reactive dyes, conversely, are used for cellulose fibres, as they form a covalent bond with the substrate. Physical-chemical classification of synthetic dyes is done based on their chromophore groups. The chromophore group is responsible for light absorbance and the consequent colouration phenomena (Gul et al., 1984). The physical-chemical classification of synthetic dyes includes azo, anthraquinone, nitroso, and triphenylmethane dyes, among others. Synthetic dyes like azo dyes are the most widely used in worldwide and contain at least one nitrogen-nitrogen double bond as part of the chromophore group.

The solubility of synthetic dyes in water also plays a significant role in their classification. Some synthetic dyes are water-soluble, while others are not. Solubility characteristics are essential in determining their use in various substrates. For example, basic dyes are not water-soluble and are used to colour molecules with acidic groups, such as proteins, nucleic acids, and synthetic polymers. Thus, the classification of synthetic dyes relies on various factors, including chemical structure, principal substrate, physical-chemical type, and solubility in water. These classifications help to determine their application in different industrial sectors. As the market demand for synthetic dyes increases, their variety and use will continue to evolve and adapt to changing needs.

2.4 CONGO RED DYE

Congo red, a synthetic compound of two molecules of naphthenic azo groups bonded to a single benzidine to form an acid was developed in 1884 by German scientist Paul Bottiger as a pH indicator. The chemical name was sodium salts of benzidinediazo-bis-1-naphtylamine-4-sulphonic. Thus, the chemical structure is $C_{32}H_{22}N_6N_{a2}O_6S_2$. Hence the pH is below 3, and it has a blue-violet appearance. However, it turns red when the pH exceeds 5 and loses its odor. Activated carbon or hydrocarbons adsorbent can be used to easily remove Congo red through adsorption because of its high solubility in water.

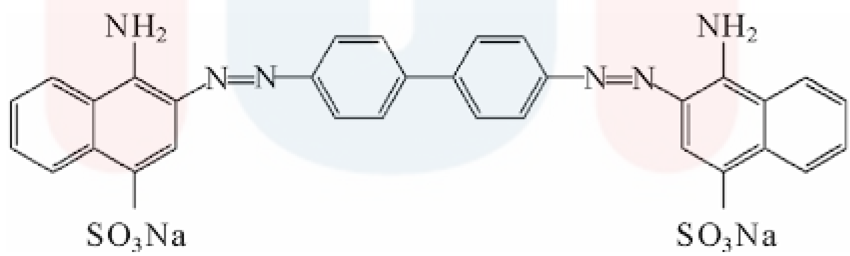


Figure 2.2: Chemical structure of Congo dye ($C_{32}H_{22}N_6N_{a2}O_6S_2$) (Source: Alam et al.,2015)

It is commonly used in the medical sector to diagnose amyloid and in various industries such as textile, printing, leather, paper, pulp, and cosmetics. However, its overuse in dyeing processes pollutes the environment, and its aromatic structure makes it difficult to degrade using traditional methods. More studies are needed for its removal from wastewater.

2.5 PREVIOUS RESEARCH ON CONGO RED REMOVAL

Researchers have recently investigated various adsorbents to remove Congo red from wastewater. Several studies related to Congo red removal from Table 2.5 with examples of adsorbent, adsorbate, adsorption capacity (mg/g), and reference. Table 2.5 shows below used Sugarcane bagasse, an agricultural waste, has the ability to adsorb red dye when used as an adsorbent of 62.5 mg/g was achieved. The study claimed that the sugarcane bagasse adsorbent effectively removed Congo red from wastewater owing to its substantial specific surface area and elevated porosity, making it capable of interacting with the dye molecules (Karmaka et al., 2020). Another case explored using low-cost adsorbents derived from natural materials like bamboo leaves for Congo red removal from wastewater. This study found that bamboo leaf-derived adsorbents achieved a capacity for adsorption of 75.75 mg/g. Not just that, the commercial activated carbon recorded of adsorption capacity of a higher rate, which is 493.8 mg/g, than another adsorbent. This is due to the activated carbon's high porosity and surface area (Yang et al., 2010). The researchers suggested implies Congo red's adsorption over to bamboo leaves' surfaces was due to various interactions like hydrogen bonding and electrostatic interactions (Sigh et al., 2020).

Table 2.5: Previous research on Congo Red removal

Adsorbents	Adsorbate	Adsorption Capacity (mg/L)	References
Sugarcane Bagasse	Congo Red	62.5	(Karmaka et al., 2020)
Bamboo Leaves	Congo Red	75.75	(Sigh et al., 2020)
Commercial Activated Carbon	Congo Red	493.8	(Kannan et al., 2001)

In conclusion, removing Congo red from wastewater is crucial for preserving our planet. Various studies have discovered different adsorbents like sugarcane bagasse, bamboo leaves, and commercial activated carbon to mitigate this problem. These studies showcase the efficient adsorption capacity of these low-cost adsorbents, which can be significant to the economic and environmental sustainability of wastewater treatment processes.

2.6 BIOCHAR

Biochar is a solid material obtained through the thermal decomposition of organic waste materials in an oxygen-limited environment (Liu WJ et al., 2019). This pyrolysis process involves heating biomass at high temperatures (typically between 300 and 700°C) without oxygen (Pariyar P, Kumari K, Jain MK, et al., 2020). Pyrolysis not only produces biochar but also yields bio-oil and syngas, which are valuable by-products that can be utilized as energy sources (Kim S, Lee Y, Lin KYA, et al., 2020)

The properties and quality of biochar depend on several factors, including the type of feedstock, pyrolysis conditions (temperature and heating rate), and post-processing methods (Corwin CH., 2008). Some common feedstocks for biochar production include agricultural residues, forestry waste, and municipal solid waste (Lehmann J, Joseph S., 2015). The choice of feedstock significantly affects the physicochemical properties of the resulting biochar, such as its elemental composition, surface area, and porosity (Weber K, Quicker P., 2018).

2.7 MANGOSTEEN *GARCINIA MANGOSTANA* PEEL AS AN ADSORBENT

Mangosteen peel is an attractive material for use as an adsorbent due to its abundant, low-cost, and renewable nature. The peel contains various active compounds, including xanthones, flavonoids, and tannins, giving it a high adsorption capacity. Researchers have investigated its potential for removing multiple pollutants, including heavy metals, dyes, and organic compounds. One study cited in the article by Chowdhury et al. (2019) investigated the use of mangosteen peel for the removal of toxic hexavalent chromium (Cr (VI)) from aqueous solutions. The results showed that the peel had a high adsorption capacity for Cr (VI), with an efficiency of up to 91.9% at an initial 10 mg/L concentration. The study attributed this high adsorption capacity to carboxylic, hydroxyl, and phenolic groups in the peel, which enable it to form complexes with the Cr(VI) ions.

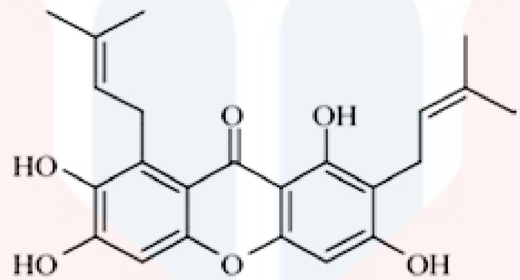


Figure 2.3: Chemical structure of Mangosteen Garcinia Mangostana peel. (Muchtaridi et al., 2017)

Another study cited by (Rattanapan et al., 2015) investigated the use of Mangosteen peel to remove methylene blue, a common dye used in the textile industry. The results showed that the peel had a high adsorption capacity for methylene blue, with an efficiency of up to 98.17% at an initial concentration of 30 mg/L. The study attributed this high adsorption capacity to the presence of carbonyl and hydroxyl groups in the peel, which enables it to form hydrogen bonds with the methylene blue molecule. Using Mangosteen peels as an adsorbent shows excellent potential for removing various pollutants from wastewater. Its low cost, renewability, and high adsorption capacity make it an attractive alternative to conventional adsorbents, which are often expensive and non-renewable (Ahmad and Alrozi., 2010).

In this area is warranted to fully explore the potential of mangosteen peel as adsorbent further research. Thus, mangosteen peel is a promising adsorbent material with a high potential for wastewater treatment. Its high adsorption capacity for various pollutants is attributed to active compounds such as hydroxyl, carbonyl, carboxylic, and phenolic groups (Selvaraju and Bakar, 2017). Despite the promising results found in several studies, more research is needed to fully understand the adsorption mechanisms and optimize the material for different types of pollutants (Khan et al., 2018). Nonetheless, mangosteen peel has the potential to be an essential contributor to sustainable wastewater treatment technologies.

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS

The Raw material is a Mangosteen peel used in this study and obtained in Kuala Lipis, Pahang.

3.1.1 The Apparatus and Equipment

The apparatus used for this experiment was a Conical flask (250ml), beaker (5ml), filter paper, microppipet 1000πL and 100 πL, Spatula, volumetric flask (100ml and 50ml), dropper, cuvette, blender, aluminium foil, and stirrer.

The equipment used in this study is a blender, oven, furnace, UV-Vis spectrometer, and FTIR spectroscopy analyzer.

3.1.2 Chemical Reagent

These chemicals and reagents required for this experiment are Congo Red dye ($C_{32}H_{22}N_6N_{a2}O_6S_2$).

3.2 METHOD

3.2.1 Preparation of (*Garcinia Mangostana)* peels

Mangosteen peel has been used as an adsorbent, and it was obtained from Kuala Lipis, Pahang. Mangosteen will be peeled, and the peels were taken and cut into small pieces. Thus, the mangosteen peel was rinsed using distilled water to remove the remaining moisture content and dried into the oven at 60˚ C for 24 hours (Li et al., 2018). After 24 hours, the dried mangosteen peel was blended into powder form and milling machine for 10 minutes per batch (Li et al., 2018). Once dried, the powder is sieved to produce uniform particle sizes of 0.125mm for adsorption. At that point, the test was put away in an air-tight zipper pack.

3.2.2 Preparation of adsorbate (Congo Red Dye) calibration curve

A Congo Red stock solution was prepared by dissolving 0.5g of Congo Red in 500 ml of distilled water. The stock solution was diluted into 0.5 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, and 30 mg/L. The dye concentration would be tested and analyzed by UV-Vis spectrometer using distilled water as a blank solution at 497 nm (Thermo Scientific, Gynesis 20) (Somasekhara Reddy and Nirmala, 2012). The concentration of the dye solution after the experiment would be determined based on the graph.

3.2.3 Removal Efficiency of Congo Red

Adsorbent mangosteen peel will sieve by using the sieved machine in various sizes. 1 g of adsorbent with different sizes with mixture of 150 ml of 100 mg/L Congo Red solution were agitated at room temperature with 150 rpm for 10 minutes. Then, left for 24 hours the mixture of adsorbent and adsorbate to obtain equilibrium. Subsequently for 24 hours, by using the filter papers the sample was filtered. Absorbance measurements were taken initially and later employing a UV-Vis spectrometer Congo red solution. Adsorption at wavelengths of 497 nm of wavelength (K.Louma et al., 2019). The percentage of Congo red removal rates was calculated using Equation 3.2.3. After calculation, the rejection rate for each run is entered into the Design Expert® software.

Dye removal in percentage: -
Percentage removal (%) = $\frac{(C_o - C_e) \times 100}{C_o}$
Percentage removal (%) = $\frac{initial\ concentration - final\ concentration}{initial\ Concentration} \times 100$ Equation 3.2.3

Table 3.1: Formula dye removal in percentage (%)

Based on the table above, where the C_o was the initial concentration of Congo Red dye in solution (mg/L), and the C_e was the final concentration of Congo Red dye in solution (mg/L).

3.2.4 Chemicals Analysis and Characterization

i. Functional group analysis

Fourier Transforms Infrared Spectroscopy (FTIR) will be used to determine the chemical of a composition ground mangosteen peel powder. Besides, the surface functional groups of the mangosteen peels were recognized using 2 mg of ground mangosteen.

3.2.5 Effect of Initial dye concentration

The ideal adsorbent size (0.125 mm) and dosage (1.5 g) had an impact on the initial dye concentration. In this research study, the initial dye concentration will range widely between 80 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L, and 300 mg/L depending on the use of the Congo Red dye solution.

3.2.6 Effect of contact time

The contact time among dye and adsorbent was examined at the ideal adsorbent size (0.125 mm), dosage (1.5 g), and initial dye concentration (30 mg/l). These parameters remain unchanged when the following parameter is set. 50 ml of dye was used, and the impact of contact time was also investigated. The outcomes in all three runs can be obtained by varying the contact time from 3 hours, 8 hours, 12 hours, 16 hours, 20 hours, and 24 hours (Kurniawati et al., 2021). Subsequently, the dye and adsorbent solution was mixed at room temperature for 10 minutes at 150 rpm. Following the specified times, the conical flasks were labeled and left undisturbed. The dye and adsorbent sample was filtered in accordance with the time recommended. The filtrate was measured at 497 nm using a UV spectrophotometer (K.Louma et al., 2019).

3.2.7 Effect of adsorbent dosage

With the adsorbent size of 0.125 mm, the greatest removal rate was achieved. chosen as the optimal value and applied to this and the following parameters. 0.5 g, 1.5 g, 2.5 g, 3.5 g, 4.5 g, and 5.5 g of sorbent were analyzed with a concentration of 50 mg/L of Congo Red dye. For ten minutes, the mixture was agitated at room temperature and 150 rpm. You should give yourself five hours to reach equilibrium. After five hours, filter the material. Using a UV spectrophotometer, measure the filtrate's wavelength at 497 nm.

3.2.8 Effect of Carbonization Temperature

1.5 g of the prepared mangosteen peel biochar was added to two 50ml volumetric flask with a different temperature which 400c and 700c. A solution containing the Congo red dye is prepared by dissolving 2500µL of the dye in 500ml of deionized water. A 50ml portion of the initial dye solution is then transferred to the two volumetric flask containing the biochar. The mixture is allowed to stand for 5 hours and the adsorption process occurs over a period of 5 hours.

CHAPTER 4

RESULT AND DISCUSSION

The adsorption of Congo red dye was carried out by using agricultural material which mangosteen peel that were collected mangosteen tree. The application of natural, cost-effective and environmental-friendly adsorbents for dye removal offers a feasible alternative to costly and frequently pollutant-intensive approaches (Ngulube, Gumbo, & Masindi, 2018). Mangosteen peel, specifically, has shown considerable potential as an adsorbent due to the high content of cellulose, hemicellulose, and lignin, materials known for their adsorptive properties (Ong et al., 2018).

4.1 CHARACTERISRIC OF MANGOSTEEN PEEL

4.1.1 FT-IR Analysis

Fourier transform infrared spectroscopy (FTIR) is an analytical method of characterising materials based on their molecular composition and structure (Thomson, J., 2018. Microscopy: Science, Process, and History. ABC-CLIO, USA). In recent years, the application of FTIR spectroscopy in understanding the biochemical content of fruit peels, specifically Mangosteen (Garcinia mangostana), has garnered significant interest (Microspectra, 2020). Mangosteen, colloquially known as the 'queen of fruits', is famous not just for its taste but also for its peel or pericarp which is a rich source of bioactive compounds. The application of FTIR spectroscopy allows for an in-depth analysis of these chemically diverse secondary metabolites (Carvalho et al., 2020). FTIR analysis of the Mangosteen peel revealed several peaks corresponding to specific functional groups. This is commonly associated with the presence of phenolic compounds, known to be abundant in Mangosteen peel (Alvarez-Parrilla et al., 2011).

Figure 4.1: The result of FT-IR spectra of mangosteen peel before and after

Analyzing an adsorbent's chemical structure is important because it helps to better understand the process of adsorption. The spectra in FT-IR of mangosteen peel before and after Congo Red dye adsorption were examined in order to comprehend better of the functional groups available on the mangosteen peel's surface. The FT-IR spectra ranged from 200 to 1600 cm−1. Figure 4.1 displays the spectrum of mangosteen peel both prior to and following adsorption.

FT-IR Adsorption of Congo Red dye was used to better understand the functional groups present on the surface of mangosteen peels. The result of FT-IR spectra of mangosteen peel before and after adsorption can be found in Figure 4. The FT-IR spectra of mangosteen peel before adsorption showed the presence of various functional groups such as hydroxyl, carbonyl, and aromatic groups (Pedraza-Chaverri et. al., 2008). After adsorption, the spectra showed a reduce in the intensity of these functional groups, this assumes that the Congo Red dye molecules were adsorbed onto the surface of the mangosteen peels through these functional groups. Intense peaks around 2360.45 cm-1 and 2089.32 cm-1 can be allocated approximately.

4.2 CALIBRATION CURVE

To generate a linear calibration curve, a few series of Congo Red solutions at various concentrations (0.5 mg/L - 30 mg/L) were prepared from a 1000 mg/L stock solution of the dye. The calibration curve is used to determine the final 30 concentration of Congo Red dye after adsorption with mangosteen peel. A calibration curve for Congo Red shown in Figure 4.2. By plotting the absorbance values against the corresponding dye concentrations, a calibration curve can be easily attainable in table 1 below.

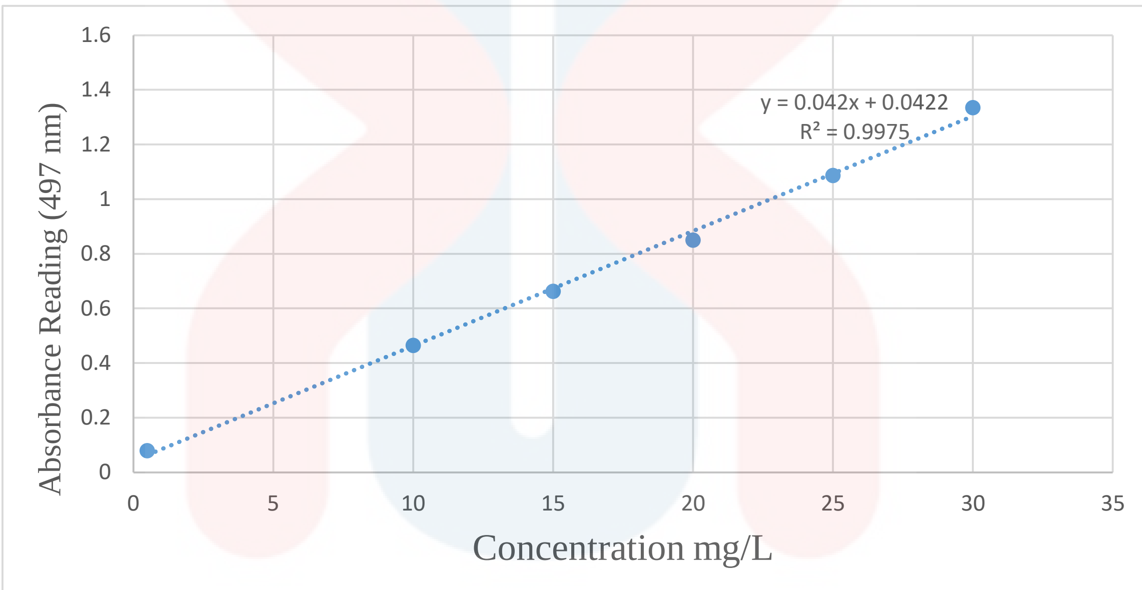


Figure 4.2: Concentration Calibration curve.

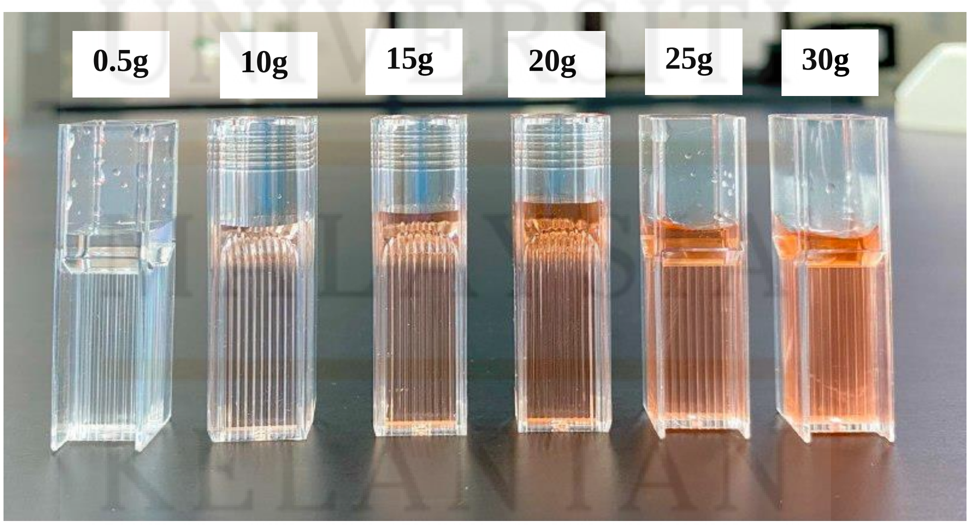


Figure 4.3: Effect of calibration curve.

Table 4.1: Standard Curve data for Congo Red Dye

Concentration mg/L	Absorbance Reading 1	Absorbance Reading 2	Absorbance Reading 3	Average Reading	Standard Deviation
0.5	0.079	0.078	0.079	0.0786	0.0004
10.0	0.465	0.466	0.467	0.466	0.0008
15.0	0.663	0.664	0.667	0.6646	0.0017
20.0	0.85	0.84	0.85	0.8466	0.0047
25.0	1.087	1.088	1.089	1.088	0.0008
30.0	1.335	1.335	1.336	1.3353	0.0004

The calibration curve shows the relationship between the concentration of a substance and the response of a measurement technique. The equation of the line ($y = 0.042x + 0.0422$) and the high coefficient of determination ($R^2 = 0.9975$) indicate a strong linear relationship between the concentration of the dye and the response of the Mangosteen Peel. This means as the concentration of the dye increases, the response of the Mangosteen Peel in removing the dye also increases in a predictable manner. The high R^2 value suggests that 99.75% of the variability in the response can be explained by the concentration of the dye. This strong correlation is important for the accuracy and reliability of the measurement technique.

4.3 EFFECT OF CARBONIZATION TEMPERATURE

The higher temperature of 700˚C promotes a faster reaction rate compared to 400˚C. According to the Arrhenius equation, the rate of a chemical reaction increases exponentially with temperature. Therefore, the higher temperature accelerates the carbonization process, leading to a more effective removal of the substance. At 700˚C, the decomposition of the organic matter is more thorough, leading to the production of biochar with a larger surface area and more micropores and mesopores (Mustafa, 2017). This increased surface area and porosity provide more active sites for adsorption, enhancing the effectiveness of the biochar as an adsorbent for Congo Red dye molecules.

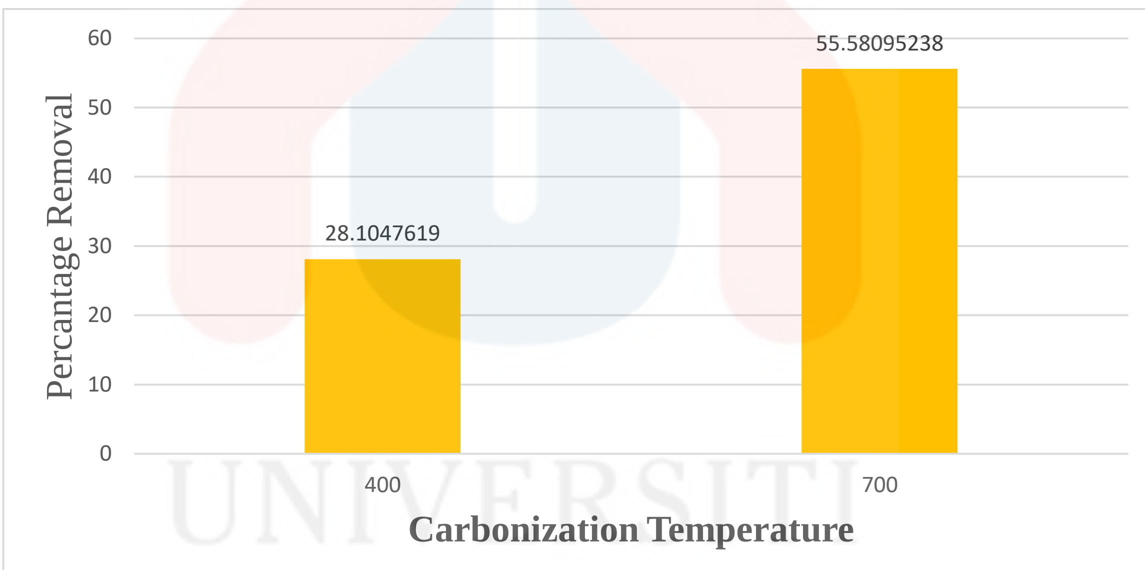


Figure 4.4: The Percentage Removal Carbonization Temperature 400˚c and 700˚c

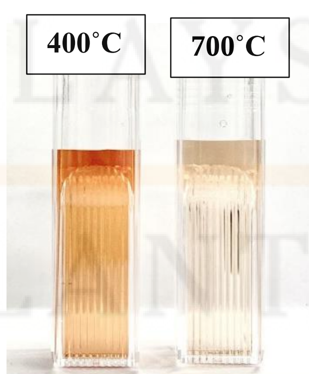


Figure 4.5: Carbonization Temperature 400˚c and 700˚c

Table 4.2: Effect of Carbonization Temperature 400˚c between 700˚c

Carbonization Temperature	Absorbance Reading	C_E	Percentage Removal %
400˚C	1.552	35.9476	28.1047
700˚C	0.975	22.2095	55.5809

Based on the graph 4.5 provided shows the percentage removal of a biochar mangosteen peel as a substance at carbonization temperatures of 400˚C and 700˚C. The data indicates that the percentage removal at 700˚C is significantly higher than at 400˚C. This can be attributed to the increased effectiveness of higher temperatures in driving the carbonization process at 700˚C, the increased temperature leads to greater thermal decomposition of the substance, resulting in higher removal percentages. This is required to the fact that biochar mangosteen peel at higher temperatures, more energy is available to break the chemical bonds in the substance, leading to increased volatilization and release of volatile components (Mustafa, 2017).

In addition, the graph's data suggests that at 700˚C, the substance undergoes more complete carbonization compared to 400˚C. This is consistent with the general principle that higher temperatures favor more complete and thorough chemical transformations. As a result, the higher temperature of 700˚C is more effective in removing the substance due to increased decomposition and carbonization because it tends to have a higher carbon content and fewer surface functional groups compared to biochar produced at 400˚C. This composition enhances the affinity of the biochar for hydrophobic contaminants like Congo Red dye, leading to greater adsorption capacity. This is attributed to the higher temperature's ability to promote greater thermal decomposition, faster reaction rates, and more complete carbonization of the substance (Corwin CH., 2017). In summary, the graph illustrates that a temperature of 700˚C is more effective than 400˚C in removing the substance through carbonization.

4.4 EFFECT OF INITIAL DYE CONCENTRATION

Figure 4 depicts the effect of initial dye concentration on congo red dye. It demonstrates how the percentage of congo red dye removal increases as the initial dye concentration decreases. Since, the efficiency of mangosteen peel as an adsorbent for dye removal that has been a subject of recent research. In a study published on IOP Science by Zhang et al. (2021), the authors investigated the efficiency of mangosteen peel for the removal of dyes. The study demonstrated that mangosteen peel shows an efficient adsorbent for the removal of dyes from aqueous solutions. The adsorption experiments were performed using the batch technique to explore the efficiency of the adsorbent. The results revealed that the percentage of dye removal was as high as 99.7% when using 5 g/L of dried mangosteen peel, highlighting its potential for highly efficient dye removal. As the initial dye concentration increases, the number of available adsorption sites on the mangosteen peel might become saturated. When all the active sites are occupied by dye molecules, further increases in concentration may not lead to a proportional increase in adsorption.

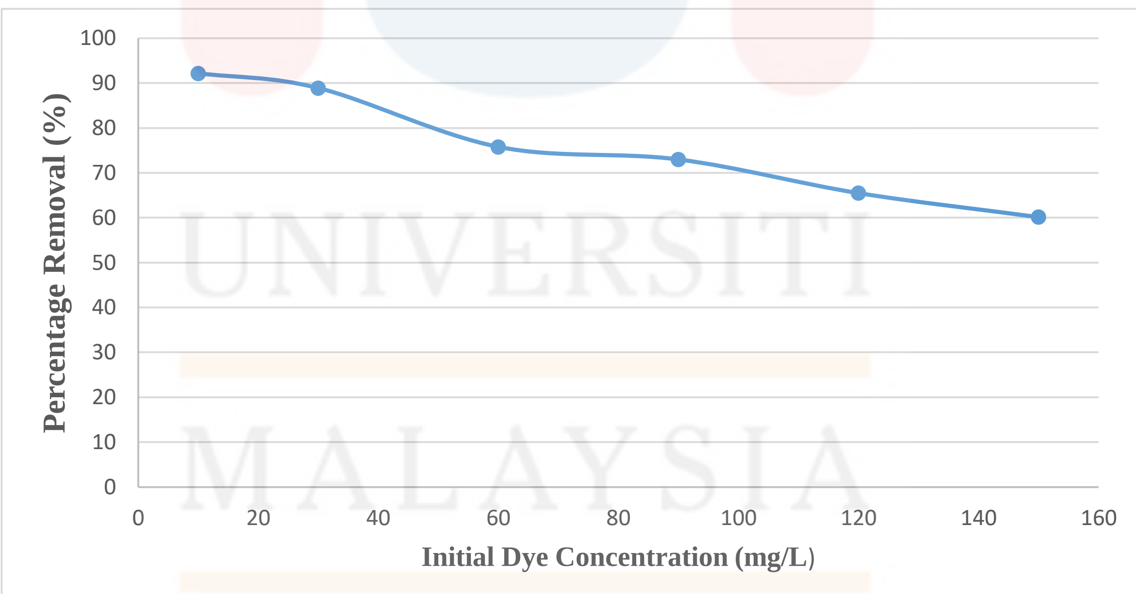


Figure 4.6: Effect of Initial Dye concentration on the removal of Congo Red dye using Mangosteen Peel

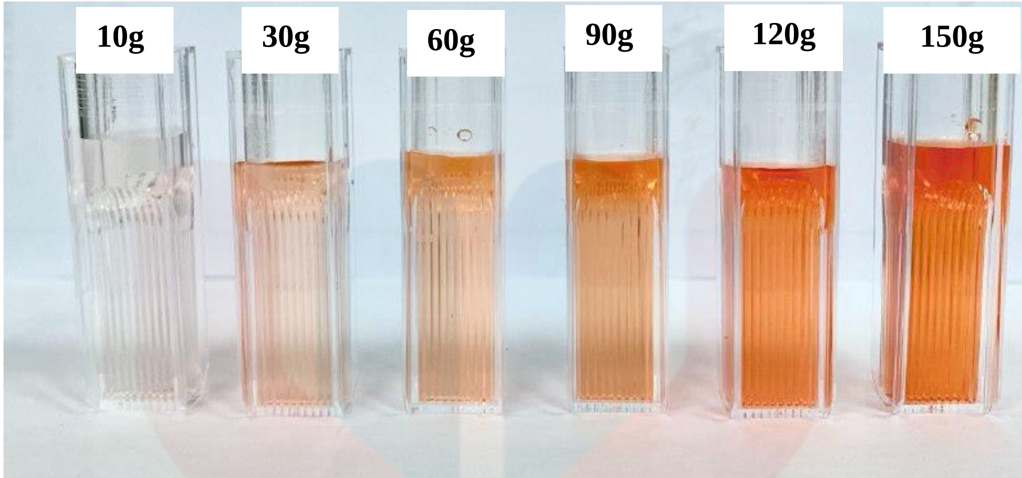


Figure 4.7: Effect of Initial Dye Concentration

The adsorption capacity of an adsorbent, such as mangosteen peel, is influenced by various factors, including the initial dye concentration (Sun et al. 2017). As the initial dye concentration increases, the percentage of dye removed may decrease due to the limited adsorption capacity of the adsorbent was closely related to its surface area. If the surface area of the mangosteen peel is limited, it may not be able to accommodate a higher concentration of dye molecules beyond a certain point. This phenomenon was observed in the study, where the percentage removal of Congo red dye decreased from 92.19mg/L to 60mg/L as the initial dye concentration increased to 150%. At higher initial dye concentrations, there might be mass transfer limitations. This means that the rate at which dye molecules can reach the adsorption sites on the mangosteen peel becomes a limiting factor at 30 mg/L.

Table 4.3: Adsorption of Congo Red dye on different initial dye concentrations

Initial dye Concentration mg/L	Absorbance Reading 1	Absorbance Reading 2	Absorbance Reading 3	Average Reading	C_E	Percentage Removal %
10	0.075	0.075	0.076	0.0753	0.7809	0.0004
30	0.182	0.183	0.184	0.183	3.329	0.0008

60	0.652	0.652	0.653	0.6523	14.519	0.0017
90	1.064	1.065	1.066	1.065	24.329	0.0047
120	1.783	1.783	1.784	1.7833	41.448	0.0008
150	2.553	2.554	2.557	2.5546	59.780	0.0004

From the table 3 above shows, as the concentration increases, the ability of the dye molecules to diffuse and be adsorbed becomes slower. Hence, there may be increased competition among dye molecules for available adsorption sites. This competition can reduce the overall efficiency of the adsorption process. The mangosteen peel may have a finite capacity for adsorbing dye molecules. Once this capacity is reached, any additional dye molecules introduced to the system may not find suitable sites for adsorption, leading to a decrease in removal efficiency. The findings highlight the importance of considering the initial dye concentration when evaluating the efficiency of mangosteen peel for dye removal.

Furthermore, the results provide valuable insights into the potential application of mangosteen peel as a low-cost and sustainable adsorbent for the removal of dyes from industrial effluents. The research contributes to the growing body of knowledge on the utilization of agricultural waste materials for environmental remediation purposes.

Hence, the study by (Zhang et al. 2021) sheds light on the efficiency of mangosteen peel for dye removal and its potential as an adsorbent for the treatment of dye-containing wastewater. The observed adsorption behavior concerning varying dye concentrations underscores the importance of optimizing the conditions for dye removal processes. The findings offer valuable implications for the development of eco-friendly and cost-effective approaches to mitigate the environmental impact of dye pollution.

4.5 EFFECT ON DOSAGE ADSORBENT IN BIOCHAR

Hence, another factor also would contribute to the effect of the percentage of Congo Red dye removal. The dosage of mangosteen Peel was able to determine the adsorbent capacity at the operation condition as shown above. The effect of mangosteen peel dosage was to provide more surface area, which meant increasing the binding site for the adsorption process, which was consistent with a previous study, as increasing the dosage of adsorbent will decrease the residual dye in the solution (He et al., 2019).

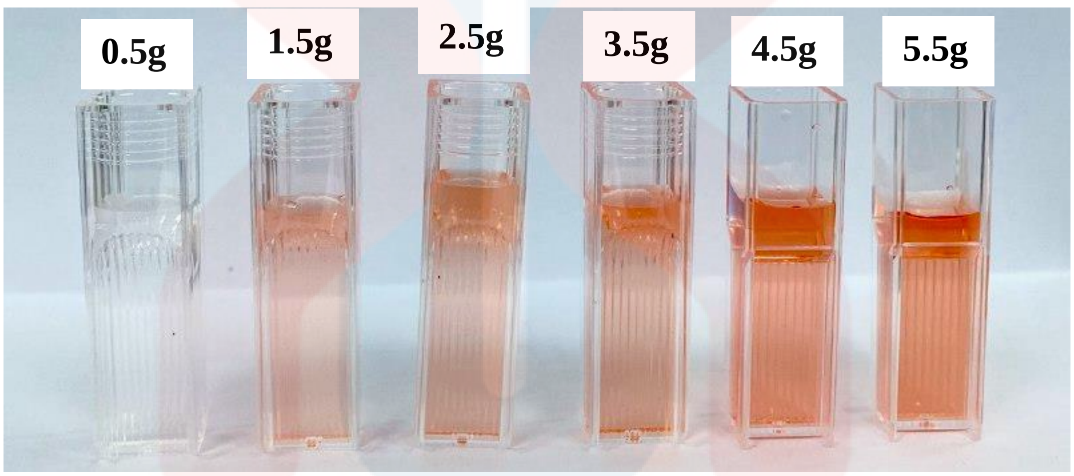


Figure 4.8: Effect of Dosage

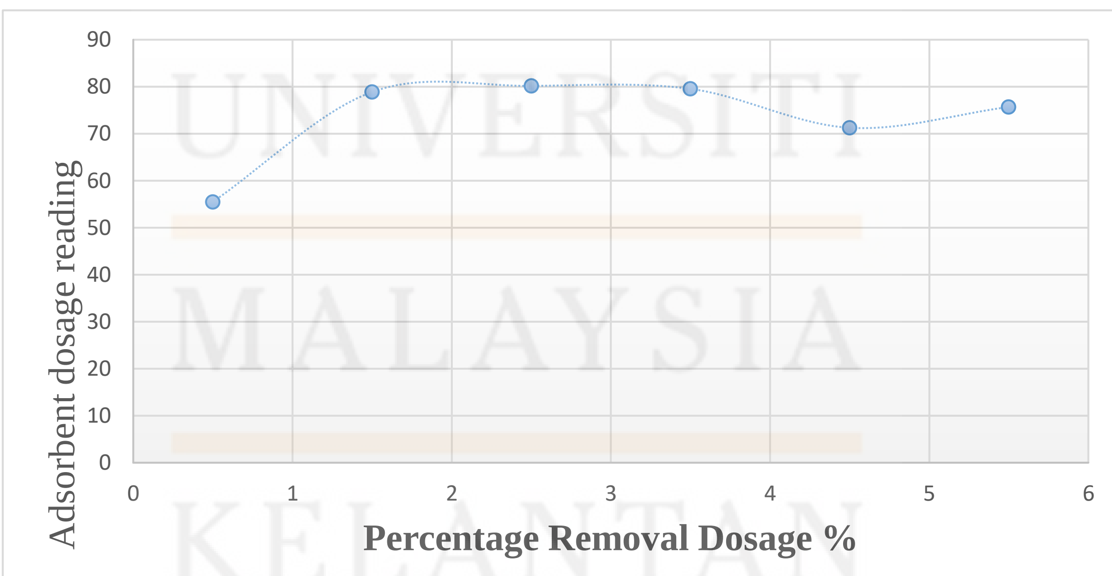


Figure 4.9: The Percentage Removal Dosage of Congo Red dye using Mangosteen Peel

Based on the figure 4.8 above was shows from 0 increased to 0.976 nm using 497 nm wavelengths. At the constant 50 mg/L initial dye concentration, the 0.5g of adsorbent dosage was able carry out around 55.53 % of Congo Red removal while increasing the dosage to 1.5 g of biochar Mangosteen Peel, the percentage of Congo Red removal was increasing nearly to 78.91 % which increasing around 23.44 %. Then, the 2.5g of adsorbent dosage was able carry out around 80.2 % of Congo Red removal was increasing approximately.

Table 4.4: Adsorption of Congo Red dye on different adsorbent dosage

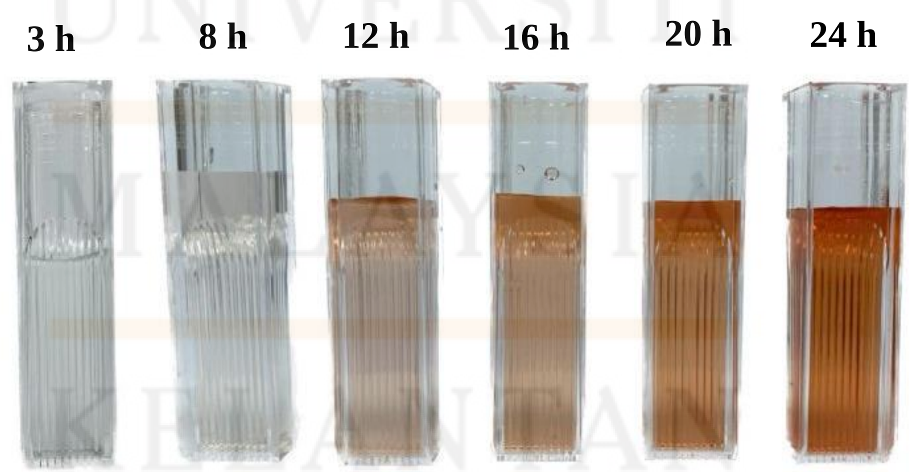
Adsorbent Dosage (g)	**Absorbance Reading 1**	**Absorbance Reading 2**	**Absorbance Reading 3**	**Average Reading**	**C_E**	**Percentage Removal %**
0.5	0.976	0.976	0.977	0.976	7.3523	55.53
1.5	0.485	0.487	0.488	0.486	24.923	78.91
2.5	0.458	0.459	0.46	0.459	42.709	80.2
3.5	0.471	0.471	0.472	0.471	70.423	79.58
4.5	0.645	0.646	0.647	0.646	70.423	71.3
5.5	0.552	0.552	0.553	0.552	70.423	75.72

Table 4 provides data on the effect of adsorbent dosage. However, the percentage of dye removal remained constant beyond 3.5 g, at around 79.58%. This is due to the overcrowding of adsorbent particles, which causes overlapping of adsorption sites. According to theory, as the adsorbent dosage increases, particles aggregate, resulting in decreased efficiency and dye uptake (Jianlong et al., 2002) stated that overlapping adsorbent particles can limit access to available surface-active sites.

Since enhancing the dosage, the dye removal did not improve significantly. The adsorbent's active site was completely saturated with the dye molecule (adsorbate), and using this adsorbent nearly resulted in the maximum percentage of dye removal. Mangosteen peel contains natural compounds such as tannins and xanthones, which can interact with the dye particles. Mangosteen peel has a high adsorption capacity. It can effectively adsorb and remove dye molecules from the solution. Thus, the adsorption rate will be reduced. The optimum dosage for Congo Red dye was 1.5 g.

4.6 EFFECT OF CONTACT TIME

An essential parameter to look into in the adsorption process is equilibrium time. The impact of contact time on the removal of Congo Red dye using mangosteen peel is evidently demonstrated in Figure 4.8. After reaching equilibrium, the percentage of dye removed decreased more slowly than it had increased massively. In the initial three to eight hours of contact, the percentage of dye removal grew steadily. Between 8 and 16 hours, the percentage of dye removed stayed almost incessant. The dye removal rate did, however, start to decline after 16 hours. Using macauba palm cake and cotton stalk, (Vieitra et al., 2012) reported similar results. According to Abdullah and Teha (2012), there has been a rise in Congo Red dye.



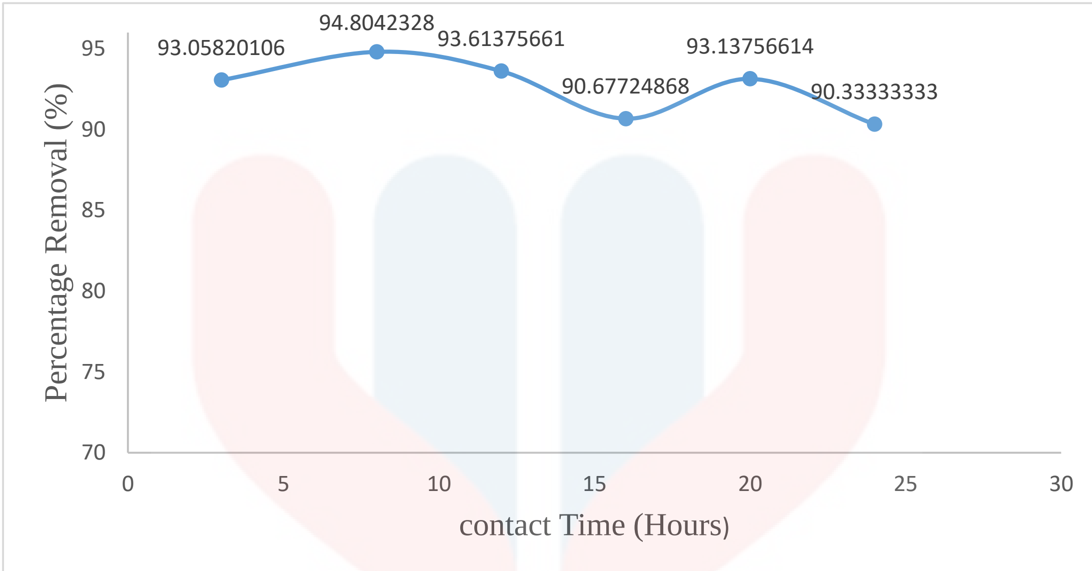


Figure 4.11: The Percentage of Removal Contact time

Table 4.5: Adsorption of Congo Red dye on different Contact Time

Contact Time (H)	Absorbance Reading 1	Absorbance Reading 2	Absorbance Reading 3	Average Reading	C_E	Percentage Removal %
3 hours	0.109	0.138	0.142	0.130	0.130	93.0582
8 hours	0.089	0.116	0.118	0.108	0.108	94.8042
12hours	0.107	0.129	0.132	0.122	0.123	93.6137
16 hours	0.142	0.168	0.169	0.160	0.160	90.6772
20 hours	0.115	0.134	0.137	0.129	0.129	93.1375
24 hours	0.152	0.169	0.171	0.164	0.164	90.3333

Based on table 5 above shows the percentage removal of the dye at different contact times. The graph indicates that the percentage removal of Congo red dye increases with the contact time, reaching a peak around 8 hours, and then starts to decrease. This trend is in line with the general understanding that the efficiency of the adsorption process and the adsorption capacity typically increase with contact time, allowing for the diffusion and adhesion of the adsorbate molecules to take place. However, prolonged contact can lead to decreased adsorption due to the saturation of active sites on the adsorbent, causing a decline in efficiency and adsorption capacity (Mohamed Danish et al., 2019).

The graph shows that the percentage removal of Congo red dye increases with the contact time, reaching a peak around 8 hours, and then starts to decrease. This trend is in line with the general understanding that the efficiency of the adsorption process and the adsorption capacity typically increase with contact time, allowing for the diffusion and adhesion of the adsorbate molecules to take place. However, prolonged contact can lead to decreased adsorption due to the saturation of active sites on the adsorbent, causing a decline in efficiency and adsorption capacity (et al Mohamed Danish., 2019).

The optimum contact time for adsorbing Congo red dye using mangosteen peel as an adsorbent can be determined through experimental studies, and it is an important parameter to consider in the adsorption process (et al Asma., 2019). Therefore, based on the graph, the optimal contact time for the adsorption of Congo red dye using mangosteen peel as an adsorbent appears to be around 8 hours, as this is where the percentage removal is highest. Contact time significantly affects Congo red dye adsorption using mangosteen peel, with optimal adsorption at 8 hours.

4.7 ADSORPTION ISOTHERM

The significance of adsorption isotherm studies lies in their ability to reveal the distribution of adsorbent molecules between the liquid and solid phases at the equilibrium state of the adsorption process. According to Ola et al. (2005), it is the equilibrium relationship between the amount of adsorbate removed and the amount left. Determining whether the adsorption process takes place on the adsorbent's heterogeneous or homogeneous surfaces is another benefit of adsorption isotherm research. The adsorption isotherm study in this work was conducted using the Freundlich and Langmuir isotherms.

Table 4.6: Langmuir and Freundlich adsorption isotherm parameters for Initial dye concentration and contact time.

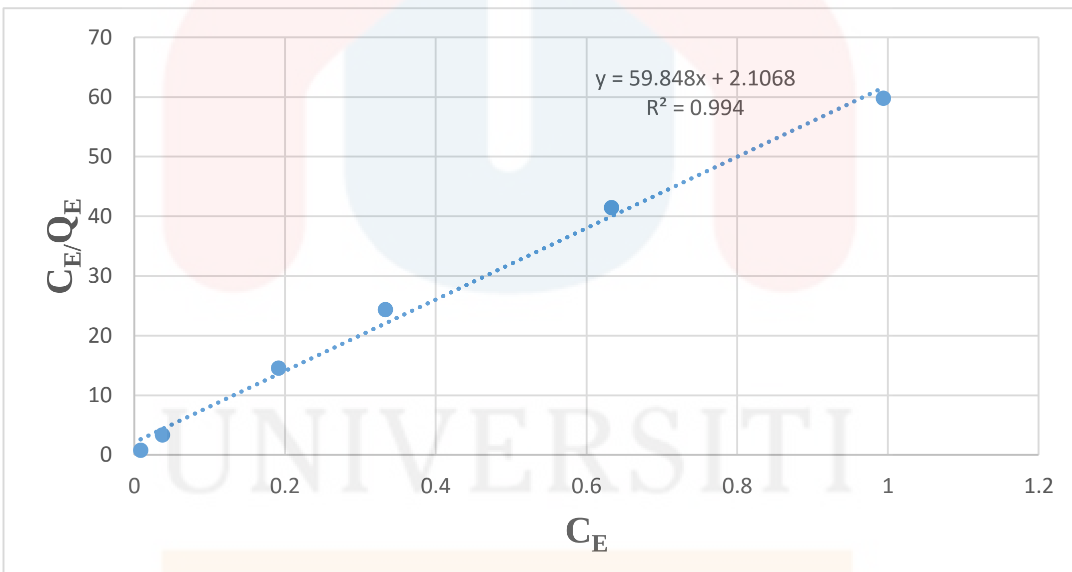
Adsorption Parameter	Langmuir Adsorption isotherm parameters			Freundlich Adsorption isotherm parameters		
	Qmax (mg/g)	**K_L (L/mg)**	**R^2**	**K_F**	**n**	**R^2**
Initial Dye Concentration	0.0167	28.4070	0.994	3.058	-10.395	0.911
Contact Time	85.47	-5.85	0.9998	3.5553	-12.5470	0.9902

The Langmuir model is characterized by the parameters Qmax and K_L, table 4.2 representing the maximum adsorption capacity and the energy of adsorption, respectively. The Freundlich model, on the other hand, is described by K_F and n, which denote the adsorption capacity and intensity of adsorption, respectively. The R^2 values associated with the Langmuir and Freundlich models for initial dye concentration and contact time are 0.994 and 0.911, and 0.9998 and 0.9902, respectively.

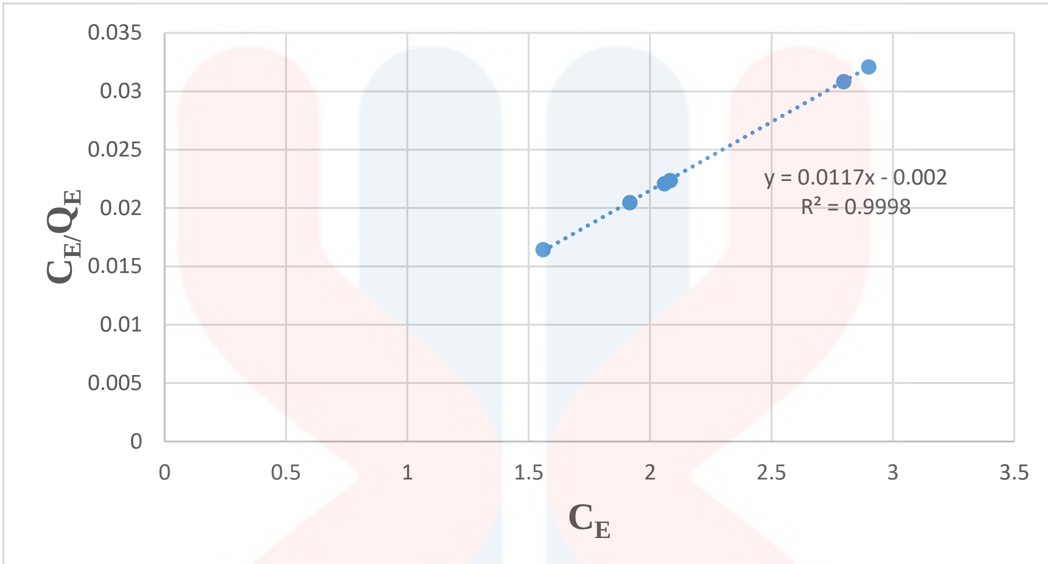
These R^2 values indicate the goodness of fit of the models to the experimental data. A value closer to 1 suggests a better fit. The provided graphs further illustrate the fitting of the Langmuir and Freundlich models to the experimental data. The Langmuir model demonstrates a high degree of fit (R^2 = 0.9998) for the adsorption of congo red dye on biochar from mangosteen peel as a function of contact time. Similarly, the Freundlich model also exhibits a good fit (R^2 = 0.9902) for the same adsorption process concerning contact time. The Langmuir and Freundlich adsorption provide insights into the adsorption of Congo red dye on mangosteen peel biochar, with the Langmuir model showing a slightly better fit. Indicating a monolayer adsorption process according to Langmuir, while the Freundlich isotherm suggests a multilayer adsorption process. This suggests that monolayer adsorption dominates, aligning closely with the assumptions of the Langmuir model. The difference in R^2 values supports the idea that the adsorption process is more consistent with monolayer coverage on the biochar surface.

In the Freundlich adsorption, n represents the intensity of adsorption, which reflects the degree of nonlinearity in the adsorption process. A higher value of n indicates stronger adsorption, while a lower value suggests weaker adsorption. R^2 represents the goodness of fit of the model to the experimental data, indicating how well the model describes the adsorption behavior. A higher R^2 value indicates a better fit, suggesting the model can accurately predict adsorption behavior. Both n and R^2 values are important in understanding adsorption behavior and evaluating the suitability of the Freundlich model.

The Langmuir isotherm is the basis for the maximum adsorption capacity, according to the data. It has been demonstrated that the uniform surfaces of the mangosteen peel are the site of the monolayer adsorption of Congo red dye. This investigation yielded a maximum adsorption capacity of 85.47 mg/g.

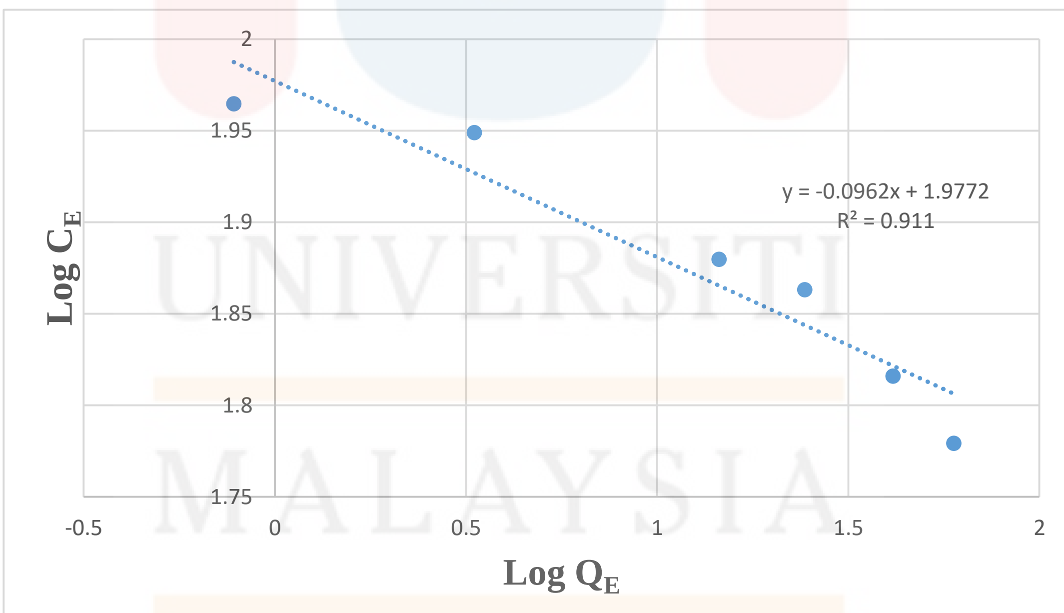


(a)

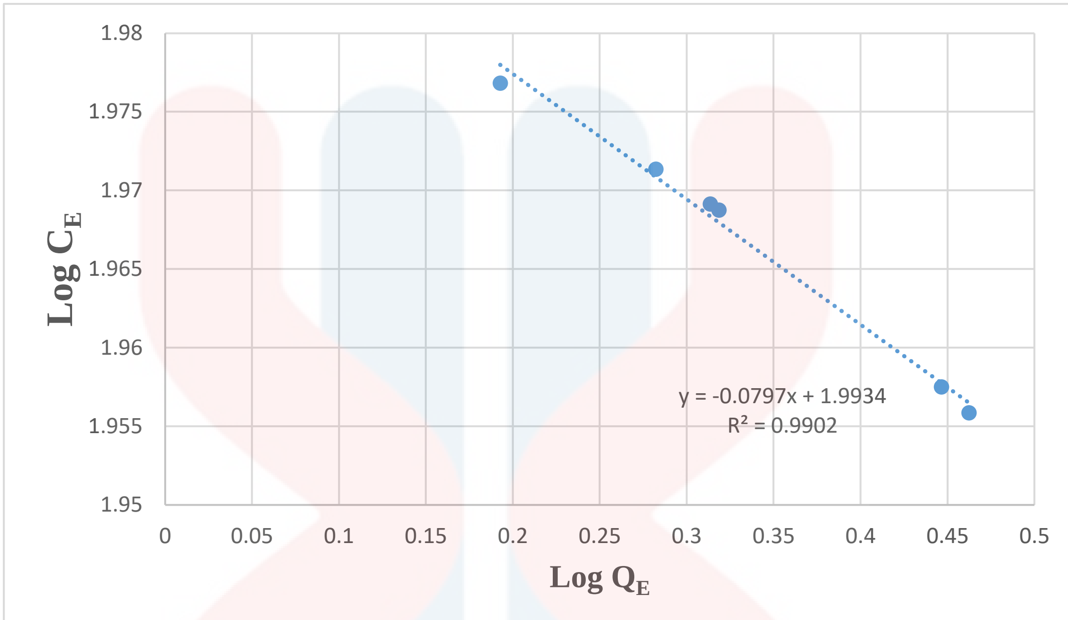


(b)

Figure 4.12: Langmuir adsorption isotherm plot for Initial Dye Concentration (a) and Contact Time (b)



(a)



(b)

Figure 4.13: Freundlich adsorption isotherm plot for Initial Dye Concentration (a) and Contact Time (b)

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Based on this study it can be conclude that the biochar is adsorbent that can be used in adsorption mechanism for removal of organic contaminant especially in removal of cationic dye such Congo red dye. The whole research demonstrated the potential of mangosteen peel as an inexpensive adsorbent to remove Congo red dye from an aqueous solution. FT-IR characterization of the mangosteen peel were not allowed for the identification of its functional groups and porous structure.

Besides, an effect of carbonization higher temperature of 700˚C promotes a faster reaction rate compared to 400˚C. This enhance surface area as well as porosity provide more active sites of adsorption activity, enhancing the efficiency of the biochar as an adsorbent for Congo Red dye molecules. Afterwards, an ideal dosage for the adsorption of Congo red dye was 1.5 g, which was the result of the adsorbent's effect. Research indicated that until equilibrium has been reached, the percentage of dye removal increased with the adsorbent dosage.

Furthermore, that whole data proved that as the initial dye concentration increased, though did the percentage of dye removal. The best concentration in this experiment to absorb 1.5 g of absorbent was 30 mg/L. Up until it reached equilibrium, the percentage of dye removal increased concurrently with contact time. The percentage of dye removal remained relatively constant for 16 hours before declining. This circumstance suggested that 8 hours was the ideal amount of adsorption. Adsorption equilibrium of Congo Red dye on mangosteen peel was described using the isotherm models. The Freundlich isotherm, the data were in good agreement with the Langmuir isotherm. 85.47 mg/g was the highest recorded, and the R2 value was close to 1.

5.2 Recommendation

Some recommendations to enhance this research for additional study are made in light of this study. Initially, it recommended assessing the mangosteen peel's capacity for adsorption in the removal of Congo Red dye from waste effluents from various industrial processes. It would provide light on how the adsorbent works and how its adsorption mechanism is affected by other elements found in the effluents. To produce quality pyrolysis conditions for biochar production from Garcinia mangostana peel, carry out additional research. Determine which residence times, heating rates, and pyrolysis temperatures, will allow the biochar to absorb the most Congo Red dye by maximizing its adsorption capacity. To assess the affordability, viability, and scalability of employing biochar as an environmentally friendly and economically viable adsorbent for the treatment of dye-contaminated wastewater, conduct pilot-scale studies. According to Senthil et al. (2013), surface modifications of the adsorbents should be done, and their effectiveness for removing dye needs to be assessed.

Furthermore, X-ray fluorescence (XRF) and Brunauer-Emmett-Teller (BET) should be used to characterize mangosteen peel. The elements in the mangosteen peel can be analyzed using XRF, and the surface area and pore sizes can be investigated using BET. To sum up, a continuous system can be used and the recovery study may be conducted in the future.

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APPENDIX A

DATA ANALYSIS

A1: Equilibrium adsorption capacity for Congo Red dye at different contact time

Contact Time (H)	C_E	Q_E	C_E/ Q_E	Log C_E	Log Q_E
3 hours	2.083	93.058	0.022	1.968	0.318
8 hours	1.559	94.804	0.016	1.976	0.192
12hours	1.916	93.614	0.020	1.971	0.282
16 hours	2.797	90.677	0.030	1.957	0.446
20 hours	2.059	93.137	0.022	1.969	0.313
24 hours	2.9	90.333	0.032	1.955	0.462

A2: Equilibrium adsorption capacity for Congo Red dye at different initial dye concentration

Initial dye Concentration mg/L	C_E	Q_E	C_E/ Q_E	Log C_E	Log Q_E
10mg/L	0.78	92.19	0.00847	-0.107	1.964
30mg/L	3.328	88.903	0.03	0.522	1.948
60mg/L	14.519	75.801	0.19	1.161	1.87
90mg/L	24.328	72.967	0.33	1.386	1.863
120mg/L	41.447	65.46	0.63	1.617	1.815
150mg/L	59.78	60.146	0.99	1.776	1.779