



Faculty of Engineering

**Synthesis of Coconut Husk-derived Carbon-based Material for
Methylene Blue Dye Removal**

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Synthesis of Coconut Husk-derived Carbon-based Material for Methylene Blue Dye
Removal

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ABSTRACT

Industrial pollution continues to represent a significant environmental challenge, as the reckless discharge of pollutants into water bodies and the atmosphere poses substantial threats to ecological systems and human health. Among the various classes of waterborne contaminants, dyes represent a particularly persistent and hazardous pollutant. Despite the development of numerous wastewater treatment techniques aimed at mitigating dye pollution, many existing methods either generate secondary pollutants or require extended treatment durations, thereby limiting their efficiency and sustainability. In this study, a carbon-based adsorbent was successfully synthesized from coconut husk using a modified Hummer's method for the effective removal of methylene blue dye from aqueous solutions. Scanning Electron Microscopy (SEM) analysis confirmed the porous nature of the synthesized material, while Energy-Dispersive X-ray Spectroscopy (EDX) characterization post-adsorption revealed a compositional shift to 62.51% of carbon, 3.04% of nitrogen, 30.15% of oxygen, 0.70% of sulfur, 0.82% of chlorine and 2.78% of iron. The adsorbent demonstrated a noteworthy methylene blue dye removal efficiency of 67.65% accompanied by an adsorption capacity of 10.15 mg/g and a final solution pH of 10. At an adsorbent dosage of 0.1 mg/L, the removal efficiency was recorded at 41.92%, thereby demonstrating the concentration-dependent nature of the adsorption process. Additionally, an increase in temperature was observed to enhance the adsorption rate, including the endothermic nature of the process. The adsorption kinetics exhibited a gradual increase in dye removal over time, ultimately achieving equilibrium within 24 hours. Isotherm modelling and kinetic studies demonstrated that the adsorption mechanism followed the Langmuir isotherm model, suggesting monolayer adsorption on a homogeneously distributed active surface. The pseudo-second-order kinetic model exhibited the strongest correlation with experimental

data, thereby substantiating that the adsorption process is predominantly governed by chemisorption. These findings underscore the potential of coconut husk-derived carbon-based material as an effective, cost-effective, and sustainable alternative for the treatment of dye contaminated wastewater.

Keywords: Carbon-based material, coconut husk, methylene blue, adsorption, kinetic study, adsorption isotherm, thermodynamic study

Sintesis Grphene Oxide Terhasil Sekam Kelapa untuk Penyingkiran Pewarna

ABSTRAK

Pencemaran industri terus mewakili cabaran alam sekitar yang ketara, kerana pembuangan bahan pencemar yang melulu ke dalam badan air dan atmosfera menimbulkan ancaman besar kepada sistem ekologi dan kesihatan manusia. Di antara pelbagai kelas bahan cemar bawaan air, pewarna mewakili bahan pencemar yang berterusan dan berbahaya. Di sebalik pembangunan pelbagai teknik rawatan air sisa yang bertujuan untuk mengurangkan pencemaran pewarna, banyak kaedah sedia ada sama ada menjana bahan pencemar sekunder atau memerlukan tempoh rawatan lanjutan, dengan itu mengehadkan kecekapan dan kemampuannya. Dalam kajian ini, penjerap berasaskan karbon telah berjaya disintesis daripada sabut kelapa menggunakan kaedah Hummer yang diubah suai untuk penyingkiran pewarna biru metilena yang berkesan daripada larutan akueus. Analisis Mikroskop Elektron Pengimbasan (SEM) mengesahkan sifat berliang bahan yang disintesis, manakala pencirian Spektroskopi X-ray Energy-Dispersive (EDX) selepas penjerapan mendedahkan anjakan komposisi kepada 62.51% karbon, 3.04% nitrogen, 30.15% oksigen, 0.70.8% sulfur, 2.8% sulfur, 0.70% klorin dan 2.8%. besi. Bahan penjerap menunjukkan kecekapan penyingkiran pewarna biru metilena biru yang patut diberi perhatian sebanyak 67.65% disertai dengan kapasiti penjerapan 10.15 mg/g dan larutan akhir pH 10. Pada dos penjerap 0.1 mg/L, kecekapan penyingkiran direkodkan pada 41.92%, proses penyingkiran yang bergantung kepada proses penjerapan. Di samping itu, peningkatan suhu diperhatikan untuk meningkatkan kadar penjerapan, termasuk sifat endotermik proses. Kinetik penjerapan mempamerkan peningkatan beransur-ansur dalam penyingkiran pewarna dari semasa ke semasa, akhirnya mencapai keseimbangan dalam masa 24 jam. Pemodelan isoterma dan kajian kinetik menunjukkan bahawa mekanisme penjerapan mengikuti model

isoterma Langmuir, mencadangkan penjerapan monolayer pada permukaan aktif yang diedarkan secara homogen. Model kinetik pseudo-second-order mempamerkan korelasi terkuat dengan data eksperimen, dengan itu membuktikan bahawa proses penjerapan sebahagian besarnya dikawal oleh chemisorption. Penemuan ini menggariskan potensi bahan berasaskan karbon terbitan sabut kelapa sebagai alternatif yang berkesan, kos efektif dan mampan untuk rawatan air sisa tercemar pewarna.

Kata kunci: *bahan berasaskan karbon, sabut kelapa, metilena biru, penjerapan, kajian kinetik, isoterma penjerapan, kajian termodinamik*

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CHAPTER 1

INTRODUCTION

1.1 Study Background

Industrial pollution is a significant issue in many areas and dumping it into water or gas at random would damage both the environment and the human body. Each country has set its emission objectives, yet the emission of some persistent industrial pollutants periodically surpasses them (Tollefson & Gilbert, 2012). Among the various forms of water contaminants, dye is a prominent polluter (Wong et al., 2003). The demand for colourants across a variety of industries, including paper, cosmetics, plastics, textiles, leather, and food, has surged in recent years, driven by expanding industrial applications and consumer preferences (Ayad & El-Nasr, 2010). The discharged coloured effluent from these sectors may provide an eco-toxic concern as well as the risk of bioaccumulation such as carcinogenic action and mutagenic action to aquatic biota and humans (Ayad & El-Nasr, 2010). As a result, industries must deal with the challenge of eliminating dyes from wastewater to an acceptable level before discharging them into the natural environment. Methylene blue which is a cationic dye that has multiple applications such as in chemical indicators, dyes, and biological staining. The printing and dyeing industries generate significant volumes of organic dye wastewater, which is characterized by intense coloration, high concentrations of organic matter, and limited biodegradability. This wastewater has a significant impact on the health of water bodies and the photosynthetic activities of microorganisms in aquatic environments.

At present, numerous strategies have been used to reduce pollutant emissions from wastewater, including adsorption, precipitation, distillation, electro-winning, reverse

osmosis, electro-coagulation, ion exchange, and cementation (Tohamy et al., 2020). Among these approaches, adsorption is considered to be one of the most appealing and significant as one of the most efficient, simple to run, and cost-effective procedures applied for the treatment of effluents containing various types of dyes (Banerjee et al., 2015). Furthermore, adsorption can retain contaminants at final concentrations lower than ppb, resulting in superior water quality (Wang et al., 2019). Pollutants can be removed from water by either directly adding adsorbents to the contaminated water or by using columns built with enough adsorbents and allowing contaminated water to pass through the columns (Ali & Gupta 2006). Adsorption is frequently used in industrial and portable applications such as source reduction and reclamation. Heretofore, several carbon-based applications, such as activated carbon (Yener et al., 2008), rice husk (Chowdhury et al., 2011), carbon nanotubes (Yao et al., 2010), and sawdust (Khattri & Singh, 2009), were available. The superior performance of carbon-based materials is attributed to their numerous advantageous properties, including exceptional chemical stability in both acidic or basic environments, resistance to corrosion capability, superior thermal stability, hydrophobic characteristics, ease of recovery from reaction mixtures, high surface area, excellent electrical conductivity and impressive mechanical strength. Moreover, their environmental sustainability and abundant availability render them highly desirable for a variety of applications (Khan, 2021).

Given the significance of carbon-based materials, the selection of cost-effective, efficient, and sustainable precursors is paramount. Natural and renewable bio-based raw materials present a compelling alternative, as they offer diverse compositional and porosity characteristics suitable for tailored applications. Carbon manifests in a vast array of allotropic forms, spanning from zero dimensional (0D) to three-dimensional (3D) structures, certain variants, such as graphene and its derivatives, gaining increasing prominence. The

identification of novel physicochemical properties in these advanced carbon materials has facilitated their strategic modification, paving the way for the development of specialized functional materials tailored for environmental applications (Mohapatra et al., 2023).

Coconut husks, which are primarily composed of lignin, cellulose and hemicelluloses, possess intrinsic properties that make them an excellent precursor for the production of biochar and for applications involving adsorption (Anuchi et al., 2022). Improved cellulose breakdown during pyrolysis enhances the porous architecture of the biochar, while increased lignin decomposition contributes to the development of biochar with a high specific surface area, elevated fixed carbon content, and refined aromatic structure (Jiang et al., 2020; Li et al., 2020). These compositional attributes highlight the versatility of biochar derived from coconut husks in advanced material applications.

It has been demonstrated through research that coconut husk, when used as a biomass feedstock, exhibits high volatile matter, low ash content, and moderate fixed carbon levels, which are favourable characteristics for biochar transformation (Shukla et al., 2019). The carbon content of coconut husk ranges from 45% to 51% by weight, which provides a high yield of biochar during carbonisation. Moreover, the low nitrogen content (1-2 wt %) reduces the release of harmful nitrogen oxides (NO_x) during the conversion process, thereby enhancing the material's environmental suitability (Tripathi et al., 2016).

The sorption properties of coconut husk are derived from its abundance of functional groups, including hydroxyl and carboxyl groups, which enable effective binding of pollutants. The fibrous layer of the coconut, which is processed during fibre extraction, contains a high lignocellulosic content, which enhances the coconut husk's adsorption capabilities. For instance, coconut husk adsorbents have exhibited remarkable efficacy,

achieving up to 89% copper removal from aqueous solutions (Jolly et al., 2022). Similarly, studies by Chanakya & Mahindra (2017) have underscored its capacity to remove metals like copper, nickel, and cadmium from industrial wastewater with minimal dosage of the adsorbent. These findings situate coconut husk as a prospective material for wastewater treatment.

In Malaysia, where coconut husk constitutes 33 – 35% of the fruit's weight, its abundant availability offers a practical solution to the challenges of waste management. The modification of coconut husk into high-performance adsorbents, including copper – impregnated and activated carbon variants, has been demonstrated its adaptability in various environmental applications (Kavitha & Namasivayam, 2007; Manju et al., 1998; Yuliusman et al., 2020). Furthermore, the high lignin and cellulose content in coconut husk contributes to its impressive calorific value of 18.62 MJ/kg, rendering it suitable for energy-related applications (Man et al., 2015; Pelissari et al., 2014).

Recent advancements have focused on the conversion of coconut husk into value-added adsorbents for the removal of dyes, particularly methylene blue. This demonstrates the renewable nature and consistent availability of the material (Arun et al., 2015; Emaga et al., 2011; Man et al., 2015). Extensive analysis has been conducted on adsorption mechanisms, including equilibrium, kinetics and thermodynamics, to optimise the performance of carbon-based materials derived from coconut husk. These efforts emphasise the potential of coconut husk as a sustainable and cost-effective resource for environmental remediation and the development of advanced materials.

This study aimed to develop carbon-based material derived from coconut husk using catalyst carbonization and the hummers method process, intended for the removal of

methylene blue from aqueous solutions. A straightforward method was employed to produce a value-added product (carbon-based material) from biomass specifically coconut husk. This study encompasses the optimisation of the analysis about the removal rate of methylene blue, including factors such as initial concentration of methylene blue, dosage study of the adsorbent, effect of contact time, effect temperature and thermodynamic study. The resultant carbon-based material is further characterised to determine its characteristics and applicability, and assessed for its efficacy in the removal of methylene blue.

1.2 Problem Statement

In general, the dye industries create synthetic dyes using chemical compounds that originate from intricate organic or inorganic sources because they can be produced inexpensively and applied to fabric with ease, they are manufactured in copious quantities. The dyes compromise the aesthetic appeal of water bodies by increasing biochemical and chemical oxygen demand, which leads to damage to photosynthesis, hindrance of plant growth, integration into the food chain, persistence, and bioaccumulation (Mudhoo et al., 2020). Water pollution caused by synthetic dyes, such as methylene blue (MB), is a significant environmental concern due to their toxicity, non-biodegradability, and persistence in aquatic ecosystems (Al-Tohamy et al., 2022).

Conventional methods for dye removal are often costly and inefficient, necessitating the development of sustainable and cost-effective adsorbents. The process of adsorption, utilizing cost-effective and readily available adsorbents emerges as one of the most efficient, straightforward, and economical methods for the removal of dye. This method approach presents noteworthy efficiency, cost-effectiveness, user-friendliness, and environmental

adaptability (Yang et al., 2022a). Biomass waste is recognized as a promising precursor for the production of carbon-based materials because its carbon richness, low cost, ease of access, ubiquitous, renewability, and environmental friendliness. Biomass wastes possess unique characteristics and diverse structures, such as inherently porous or hierarchically organized, which makes electrolyte penetration easier and reduces the diffusion distance. Interestingly, agricultural sectors or waste management recycle certain biomass from agricultural or regular wastes like bamboo chopsticks and straws, making the process both cost-effective and environmentally beneficial (Soffian et al., 2022). Carbon-based materials display diverse properties, including elevated surface area, multiple functional groups and porosity attributable to the versatility of carbon bonding. These properties can be markedly affected by the feedstock utilized in production. Diverse feedstocks, upon conversion into carbon compounds, will produce distinct properties and influence the adsorption capacity of the carbon-based materials. Coconut husk, an abundant agricultural waste, has the potential to be converted into a carbon-based adsorbent for dye removal. Previously research has indicated the potential of a range of coconut by-products, including desiccated husk, pith, fibre and shell, as effective adsorbents for the removal of heavy metals, dyes, inorganic anions, radionuclides, and other pollutants from water (Johari et al., 2016). Notwithstanding these encouraging findings, the employment of coconut husk, a readily accessible and low-cost resource, for particular purpose of removing methylene blue dye remains under-researched. This study aims to address this research gap by evaluating the potential of coconut husk-derived carbon-based material for the remediation of methylene blue in aqueous solution. Hence, the synthesis of such materials using efficient methods like Hummer's method, as well as the systematic study of their adsorption performance under varying conditions, remains underexplored.

To the best of the authors' knowledge, there is no published work currently exists on the synthesise of carbon-based material derived from coconut husk using Hummer's method for methylene blue removal. This novel approach addresses a critical gap in the development of alternative adsorbents for wastewater remediation and contributes to advancing sustainable practices in water treatment.

1.3 Research Gap

The synthesis and application of carbon-based adsorbents derived from agricultural waste, such as coconut husk, have shown promise for sustainable and cost-effective water treatment. However, significant research gaps remain that hinder their widespread adoption. Firstly, while Hummer's method is well-established for synthesizing graphene oxide and other carbon-based materials, its application for converting coconut husk into a carbon-based adsorbent has not been thoroughly explored. The optimization of this method for coconut husk and its impact on the adsorbent's structural and functional properties, such as surface area, porosity, and functional groups, remain underexplored.

Secondly, although some studies have investigated the adsorption of dyes onto carbon-based materials, there is a lack of systematic research on the effects of key operational parameters, such as initial dye concentration, contact time, temperature, and solution pH, on the adsorption of methylene blue (MB) using coconut husk-derived adsorbents. A comprehensive understanding of these factors is essential to optimize the adsorption process.

Finally, while adsorption isotherms, kinetics, and thermodynamics are critical for understanding the adsorption mechanism, limited studies have applied these models to coconut husk-derived adsorbents. The applicability of isotherm models (e.g., Langmuir,

Freundlich), kinetic models (e.g., pseudo-first-order, pseudo-second-order), and thermodynamic analysis for MB adsorption onto coconut husk-derived materials requires further investigation. Addressing these gaps will advance the development of sustainable, efficient, and cost-effective adsorbents for water treatment, while promoting the valorization of agricultural waste.

1.4 Hypothesis

The hypothesis for this study is:

- i. The carbon-based adsorbent derived from coconut husk will exhibit remarkable adsorption capability for methylene blue (MB) owing to it develops porous structure and surface functional groups.
- ii. The efficacy of adsorption is expected to be influenced by critical operational parameters, including initial dye concentration, contact time, pH, and temperature.
- iii. The equilibrium data are anticipated to conform to the Langmuir and Freundlich isotherm models, suggesting the presence of both monolayer and heterogeneous surface adsorption. It is hypothesised that the kinetic behaviour is expected to follow the pseudo-second-order model, indicating that chemisorption may be the dominant mechanism. Furthermore, the thermodynamic analysis is projected to reveal that the adsorption and endothermic under the studied conditions.

1.5 Research Objectives

The main focus of this project is to produce carbon-based material from coconut husk to remove the dye pollutants in the wastewater. The project, therefore, aims to accomplish the following specific goals.

- i. To synthesize the carbon-based material from coconut husk utilising Hummers method for the removal of methylene blue (MB)
- ii. To investigate the influence of initial dye concentration, contact time, temperature, and solution pH on the adsorption of methylene blue (MB) onto the coconut husk-derived carbon-based material.
- iii. To analyze the adsorption isotherm, kinetics, and thermodynamics of methylene blue adsorption onto the coconut husk-derived carbon-based material.

1.6 Scope of Study

In this study, a physiochemical graphitisation process combining sodium nitrate impregnation and Hummer's method was employed to synthesise carbon-based materials from coconut husk. The preparation parameters, including the impregnation ratio (1:0.5), temperature (20°C – 35°C) and time (7 hours), were meticulously optimised in alignment with the prescribed methodology. The resulting carbon-based material subjected to comprehensive characterisation in order to evaluate its structural and compositional properties. Advanced analytical techniques were employed, including scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) for the analysis of surface morphology and elemental composition, Fourier transform infrared spectroscopy (FT-IR) for the identification of functional groups and, Brunauer-Emmett-Teller (BET) analysis to determine surface area and porosity. The adsorptive potential of the synthesized material was appraised for the purpose of removing of methylene blue (MB) dye from aqueous solution within the confines of a controlled batch adsorption system. To elucidate the material's efficiency and mechanism in wastewater remediation, this approach aims to provide insights into practical applications and environmental relevance. The objective of this study was to systematically vary critical experimental parameters in order

to achieve the desired outcome. The parameters that were varied included pH study (pH 3-10), temperature (298 – 303 K), contact time (1524 minutes), adsorbent dosage (0.02 – 0.1 g), and initial dye concentration (5 – 25 mg/L). The investigation enabled the exploration of the adsorption equilibrium, kinetic behaviour, isotherm models and thermodynamic properties of the adsorbent.

CHAPTER 2

LITERATURE REVIEW

2.1 Background of dye pollution

Pollution from organic dyes has been a major issue around the world over the past few decades (Heidarizad & Şengör, 2016). It is determined that 10-15% of all dyes, which are utilized across multiple sectors such as paper, food, plastic, printing, textile, pulp, and tanneries are released into wastewater every year (Chen et al., 2017). As is quite common to all, these dyes have high poisonousness to humans, plants, and animals because they are refractory, and chemically and photochemically stable and spread the undesirable colour of the receiving waters (Moussavi & Mahmoudi, 2009). Seriously, they can obstruct virtually all light penetration, therefore interfering with the photosynthetic activities of aquatic organisms. Thus, effective measures ought to be taken to remove these hazardous dyes from wastewater. There is a growing body of literature that investigates dye removal through numerous techniques such as chemical, biological, and physical technologies (Hamadani et al., 2011, 2013; Robinson et al., 2001; Van de Zee & Villaverde, 2005). It is evident that, in the context of the separation techniques under discussion, adsorption is the most practicable and cost-effective (Yao et al., 2010). A series of recent studies have indicated that the removal of hazardous dyes from wastewater using different types of adsorbents, including those derived from carbon-based materials, polymer gels, clays and organic-inorganic composites has attracted a significant amount of attention in the scientific literature (Cheng et al., 2011; Cheng et al., 2013; Frini- Srasra & Srasra, 2010; Lee et al 2013; Monser & Adhoum, 2002; Ok Yoon et al., 2003; Zhang et al., 2013). Carbon-based compounds are the most suitable adsorbents among these materials because of their large specific surface

area and exceptional chemical and mechanical stability. Several low-dimensional carbon nanomaterials like graphene (Li et al., 2015; Li et al., 2014; Wang et al., 2019), fullerene (Cheng, Kan & Tomson, 2004) and carbon nanotubes (Qu et al., 2008), have recently demonstrated exceptionally high adsorption capacities for a variety of contaminants. However, the prohibitive cost and extra steps required for collection after adsorption limit the use of these tailored carbon nanomaterials (Liu et al, 2012).

2.2 Coconut husk

As seen in Figure 2.1, the fibrous husk of the coconut is used to extract coconut fiber, also referred to as coir. Coconut natural fibre is thick, gritty, and resistant (Bakiya et al., 2016). The coconut fruit yields 40% coconut husk and 30% fibre, with the remainder made up of coir (Salman Zafar 2022), see Figure 2.2. Coir (also referred to as coco peat, coir pith, coir dust and coir meal) is a by-product, of the coconut industry (Arenas et al., 2002) and made up of dust and short fibres extracted from the husk or the mesocarp of the fruit. Coir is a by-product of coconut production in most regions, and the husks are left on the fields as mulch or utilised as fertiliser due to their high potassium content (Salah & Romanova, 2017).

The common physical, chemical, and biological characteristics of coconut fibre have been extensively studied. Furthermore, coconut fibre provides a healthy combination of oxygen and water to plant roots and has a high re-wetting capability (Blok & Wever, 2008). On a dry-weight basis, husks are made up of 70% coir and 30% fibre. The yield ratios of long, medium, and short fibre are, on average, 60:30:10 (Salah & Romanova, 2017). Coconut fibre has a density of $0.67 - 10.0 \text{ g/cm}^3$, which blends well with an excellent combination of tensile strength of 120 -500Mpa, tensile strain of 20% and water adsorption of 80 – 180%

(Ali, 2011; Bujang et al., 2007). Furthermore, fibre has a fantastic property of temperature regulation and hence shows outstanding insulating characteristics.

Coir and fibre are removed from the coconut husk. It has two intriguing characteristics that make it commercially appealing. Coir is very hydrophilic as well as chemically reactive. Figure 2.3 shows a micrograph of the internal structure of coconut coir. Microscopy revealed that the interior structure of coconut coir is made up of thin hollow shells or tubes. Because of these hollow tubes, the coir can absorb 10 times its weight in water (Greer, 2009).

Over the last two decades, studies have revealed valuable information about the coconut husk's excellent effectiveness in eliminating dyes. According to (Aung & Htun, 2018), coconut husk has a high clearance rate of Congo red and methylene blue with 71.87% and 97.65%, respectively. Jain & Shrivastava (2008), along with Gupta et al. (2010) demonstrated that coconut husk serves as an effective and low-cost adsorbent. It is particularly efficient at absorbing water-soluble hazardous dyes, such as Tropaeoline 000 and Cyanosine, while simultaneously reducing the toxicity of the solution. The chemical oxygen demand can be lowered by coconut husk from 1480 mg/L to 208 mg/L.

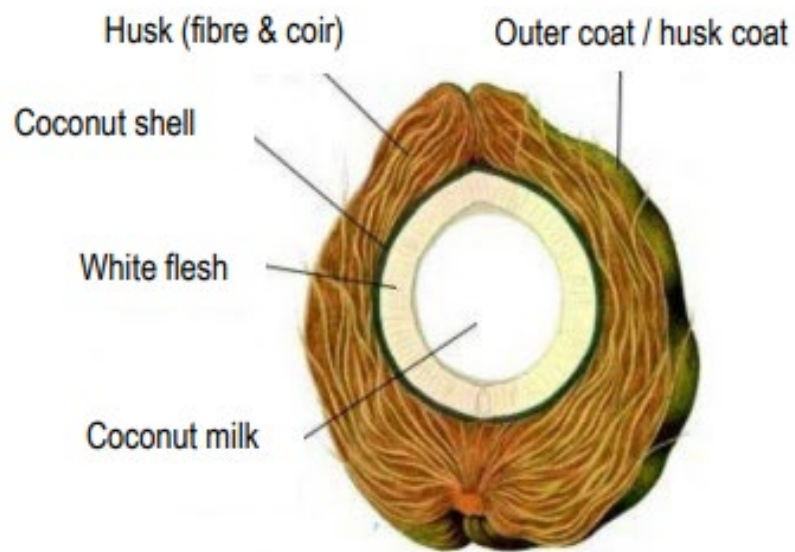


Figure 2.1: Coconut component schematics (Apse, 2017)



Figure 2.2: Coconut husk, fibre, and coir (Greer, 2008)

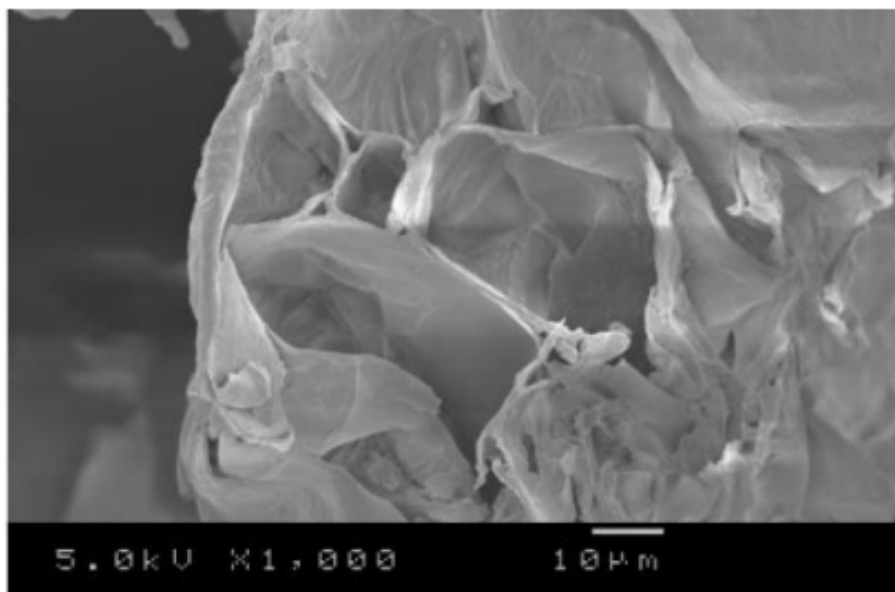


Figure 2.3: Micrograph of coconut coir structure (Greer, 2008)

2.3 Dyes

A wide variety of substances that impart colour through physical or chemical bonds with the substrate to which they are applied to are referred to as “dyes” (Giriya et al., 2022). The chromatic quality of a dye is derived from chromophores present within the molecule, which are capable of developing colour when linked to auxochromes (Kumar et al., 2021). Table 2.1 provides a categorization of dyes based on to their water solubility, ecotoxicological impacts, application, and physicochemical properties. From a structural perspective, these dyes are aromatic compounds come from hydrocarbons, including as xylene, benzene, toluene, naphthalene, and anthracene (Krivoruchko et al., 2023).

Dyes can be obtained from natural or synthetic. Natural dyes are derived from a variety of sources, including minerals, plants, animals, and different insects. In contrast, synthetic dyes are creating by humans utilising a range of organic particles (Benkhaya et al., 2020; Yaseen et al., 2019). However, the extensive use of dyes across diverse applications results in their release into the environment, frequently in conjunction with other toxic

organic or inorganic compounds derived from industrial waste, with significant implications for ecological and human health (Yaseen & Scholz, 2019). It is therefore imperative that these toxic dye and dye-laden effluents are treated effectively before they reach water sources, employing a combination of physical, chemical, and biological methods.

Dyes are classified according to a number of criteria, including their chemical structure, physicochemical characteristics, origin, and application (Rápó & Tonk, 2021). This classification also considers the potential hazards posed by toxic industrial effluents, many of which are carcinogenic, pose significant health risks and the environment pollutions (Lellis et al., 2019; Lu & Astruc, 2020). Accordingly, Table 2.1 categorises dyes such as mordant, acid, azo, basic, disperse, reactive, vat and nitro dyes, detailing their distinct properties and applications.

2.3.1 Type of dyes

Synthetic dyes are available in a diverse array of forms and frequently classified according to their molecular structure, as shown in Table 2.1. Furthermore, classification can be based on application or solubility. Examples of soluble dyes include reactive, acid, mordant and basic direct dyes while insoluble dyes encompass vat, azo, sulphur and disperse dyes (Samsami et al., 2020). Notably, azo dyes are representing the dominant market presence, accounting for 70% of global dye production and thus constituting the most widely used dye worldwide (Berradi et al., 2019; Lipskikh et al., 2018).

However, a common disadvantage associated with synthetic dyes, irrespective of their structural characteristic, is their hazardous nature (Azanaw et al., 2022). Water sources and ecosystem are seriously threatened by the discharged of untreated synthetic dyes into environment. The toxic effects of these dyes have prompted considerable concern among

environmentalists and water quality advocates. Consequently, there is a clear need for the development and implementation of effective methods and technologies for the complete and permanent remove of these dyes from water bodies (Wang et al., 2011).

Table 2.1: various types and applications of dyes

Type of dyes	Applications	Ecotoxicological effects	Examples of dyes	References
Acid dye	Textile, leather, and pharmaceutical industries; nylon, wool, silk, and modified acrylics	Vomiting, nausea, diarrhoea, carcinogenic and mutagenic effects	Acid yellow 36, Acid orange 7, Acid blue 83, Acid blue 7	(Benkhaya, M'rabet, et al., 2020; Davies et al., 2009; Seyyedi, 2006; Yamjala et al., 2016)
Basic dye	Paper, polyacrylonitrile modified nylons, and modified polyesters	Altering the chemical and physical properties of water bodies and causing determinantal effects to the flora and fauna	Methylene blue (MB), Basic red 1 or rhodamine 6G, Basic yellow 2	(Benkhaya, M'rabet, et al., 2020; Shakoor & Nasar, 2016; Vidyanagar, 2019)

Table 2.1: Continued

Direct dye	Colouring paper products	Toxic to aquatic animals and plants; carcinogenic; mutagenic, and dermatitis	Congo red (CR), Direct red 28, Direct black 38	(Benkhaya, M'rabet, et al., 2020; Jalandoni -Buan et al., 2010; Sponza & Işik, 2005; Xiao et al., 2017)
Vat dye	Cellulosic fibers, natural fibers, insoluble pigment, and indigo	Adversely impacts the quality and clarity of water resources such as lakes and rivers; rhinitis, dermatitis, and other allergic reactions	Vat acid blue 74, Vat blue 1	(Benkhaya, M'rabet, et al., 2020; Muthuraman & Teng, 2009; Vidyanagar, 2019; Yamjala et al., 2016)
Disperse	Acrylic fibers, polyester, nylon, and cellulose acetate	Carcinogenic; Mutagenic; and water and soil pollution	Disperse red 60, Disperse red 9, Disperse violet 9	(Benkhaya, M'rabet, et al., 2020; Hou et al., 1991)

Table 2.1: Continued

Nitro dye	Colorant fabric	Reduces photosynthesis activity and light penetration; carcinogenic and mutagenic	Naphthol Yellow (II)	(Benkhaya, M'rabet, et al., 2020; Raman & Kanmani, 2016)
Mordant dye	Textile fibres such as wool, silk, and leather	Shows allergic reactions	Mordant red 11, Mordant Black 17	(Benkhaya, M'rabet, et al., 2020; Kakiage et al., 2014; Shalaby & Mohamed, 2020)
Reactive dye	Dyeing cellulosic, silk, and wool fibres	High and unwater levels of dissolved solids in the effluent Allergic response in the upper respiratory tract, mucous membrane, eyes, and skin	C.I. reactive red 120, C.I. reactive red 147, C.I. reactive blue 19	(Benkhaya, M'rabet, et al., 2020)

Table 2.1: Continued

Sulphur dye	Dyeing cellulosic cotton and fibres	Blocked or itchy noses; skin irritation; sneezing and sore eyes; carcinogenic	Sulfur brilliant green, Sulfur Black 1, Leuco Sulfur Black 1, Phthalic anhydride	(Benkhaya, M' rabet, et al., 2020; Vidyanagar, 2019)
Azo dyes	Textile industry for dyeing process and food colouring	Causes carcinogenicity in humans and animals. If inhaled or swallowed, it affects the eye, skin, and digestive tract. Affects aquatic life if present in excess.	Direct Black 22, Disperse Yellow 7, Acid Orange 20, Methyl red, Methyl Orange (MO), Trypan blue	(Abid et al., 2012; Benkhaya, M' rabet, et al., 2020; Berradi et al., 2019; Manu & Chaudhari, n.d.; Yamjala et al., 2016)

2.3.2 Methylene blue

Methylene blue dye ($C_{16}H_{18}N_3SI$), a thiazine-type aromatic compound, has a molecular weight of 3199.85 g/mol, exhibits planar heterocyclic aromaticity and a distinctive

blue hue due to its cationic properties. Its application extends to the textile industry for dyeing fibres and to the medical field for staining, prophylactic, and therapeutic purposes. The physicochemical characteristics of the dye are enumerated in Table 2.2 and can be visualised in Figure 2.4 (Oladoye et al., 2022).

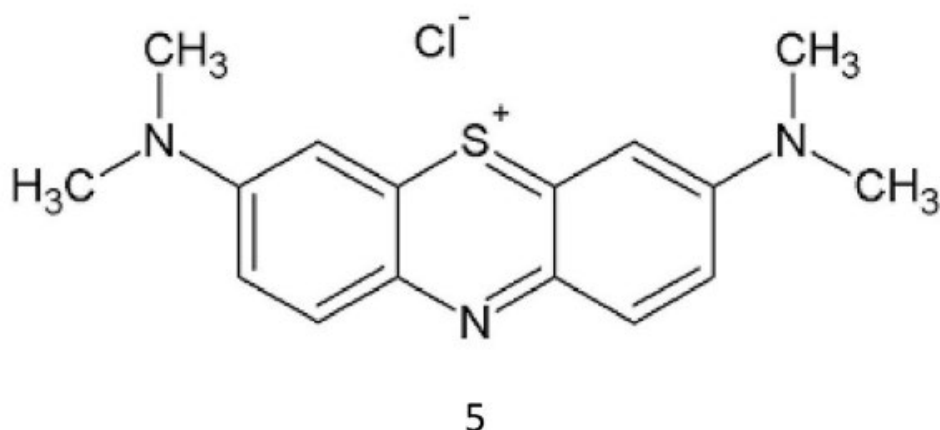


Figure 2.4: The structure of methylene blue molecular

Table 2.2: The physicochemical properties of methylene blue

Parameters	Values/ names
Maximum wavelength of adsorption (λ_{max})	664 nm
Another name	Swiss blue
Ionization	Basic
Degree of solubility	3.55%
Colour index name	Basic blue 9
Colour index number	52015
Aqueous pH	Strong acidic between pH 2.0 – 3.5

2.3.3 Impact of dyes on environment

Global textile dye production exceeds 10000 tonnes annually, with approximately 100 tonnes of dyes released into wastewater each year (Benkhaya et al., 2020). Textile industry is now the world's second most polluting sector (Bailey et al., 2022), with severe environmental consequences including the tragic desiccation of the Aral Sea, largely attributed to the excessive water use for cotton irrigation (The True Costs of Cotton: A Report by the Cotton Production and Water Insecurity, 2012).

As a result, the environmental impact of the textile industry is substantial and damaging (Lellis et al., 2019). During the dyeing process, significant amounts of synthetic dyes, which have low affinity for textile surfaces, are released into the environment, contributing to further pollution (El Jabbar et al., 2019).

The effluents from textile industry are characterised by intense colour due to the prevalent use of alkaline dye. They are also marked by high salinity and toxicity, which severely affect water quality and emit harmful waste gases (Benkhaya et al., 2020; Liang et al., 2020).

In aquatic atmospheres, dyes and their products of breakdown – which are often carcinogenic, mutagenic, and teratogenic -can partially degrade or transform in river water and sediments, creating long-lasting environmental risk (Chien et al., 2024; Wang et al., 2019). Organically bound chlorine is believed to be found in nearly 40% of dyes globally, that is a highly concerning element due to its persistence and environmental impact (Zhou et al., 2019). Furthermore, most of the dyes are resistant to deterioration due to their intricate synthetic structures, which present a significant challenge in wastewater treatment (Fritzke

et al., 2020). In fact, treating raw textile effluents is particularly challenging due to their heterogeneous composition, weak biodegradability, and toxic properties (Benkhaya et al., 2019; Rathour et al., 2019).

2.3.4 Dye removal techniques

The dyeing industry represents one of the world's largest and most essential industrial sectors. However, its wastewater discharge has been identified as a significant environmental pollutant, with a wide variety of dyes present in concentrations that threaten the integrity of local ecosystems. Some dyes have been demonstrated to possess mutagenic and carcinogenic properties (Alsukaibi, 2022; Sudarshan et al., 2023), while prolonged exposure can result in the dysfunction of kidneys, liver, brain, reproductive organs and the central nervous system in human (Dutta et al., 2024; Farhan Hanafi & Sapawe, 2020). It is therefore imperative that effective methods for the removal of dyes from wastewater are developed and implemented. Researchers are actively pursuing the development of cost-effective method to purify water that has been polluted by textile effluents, which are estimated to release approximately 280000 tons of dyes and pigments into the water systems on an annual basis (Dutta et al., 2024; Sudarshan et al., 2023).

In order to address this challenge, a range of purification methods has been developed, which can be roughly categorised into three categories: physical, chemical, and biological processes (Katheresan et al., 2018). Every technique has benefits and drawbacks when it comes to eliminating contaminants from sewage and wastewater. Figure 2.5 provides an overview of the biological, physical, and chemical processes typically employed to treat wastewater containing dyes, with the goal of making it fit for future use. Adsorption is

currently one of these highly effective techniques because of its high efficiency and affordability, and ease of application to persistent dye compounds.

A review of the literature reveals a multitude of techniques for the removal of dyes, including biological treatments, chemical oxidation, adsorption, coagulation, precipitation, and filtration with coagulation. While each method has specific advantages and disadvantages, adsorption is distinguished by its simplicity, low cost, high efficiency, and potential for recycling adsorbent materials. As evidenced by recent studies (Dutta et al., 2021), adsorption represents a practical and powerful solution for the removal of dyes from wastewater, particularly in comparison to advanced oxidation, filtration, and biological treatment process. Its adaptability, suitability for the handling of recalcitrant dye compounds, and reusability of adsorbents make adsorption a leading approach in the treatment of dye-contaminated wastewater.

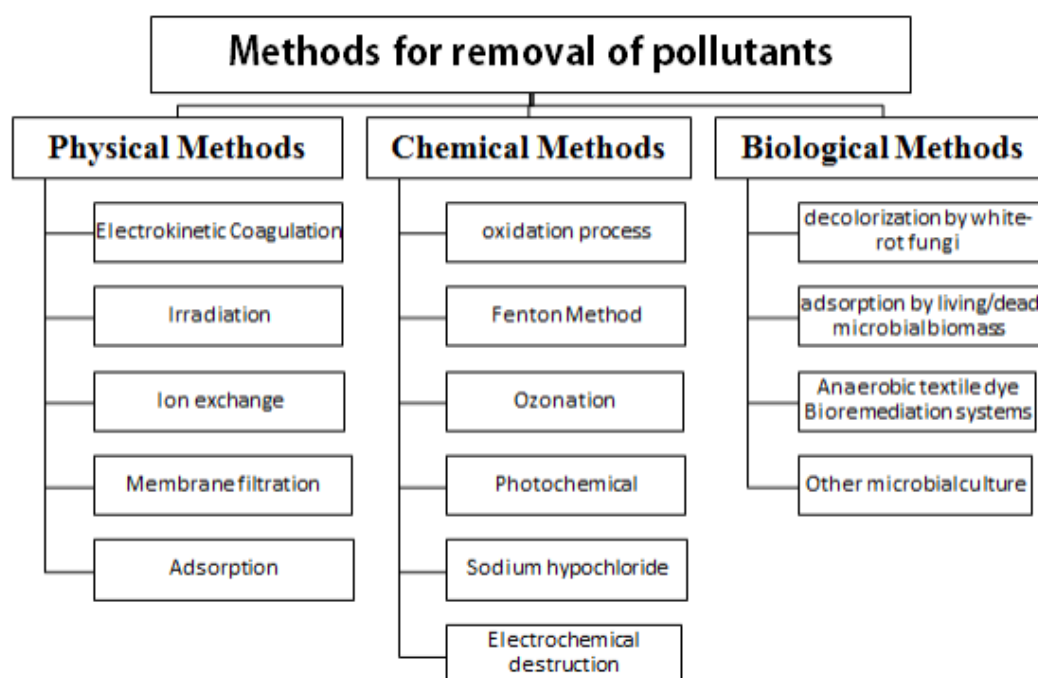


Figure 2.5: General method of removal of pollutants (Kaykhaii et al., 2018)

2.4 Adsorption

Adsorption is a surface phenomenon in whereby gas or liquid solutes, known as adsorbates, build up on the surface of an adsorbent material, such as carbon-based materials (Jideofor & Ezekiel, 2018; Sazali et al., 2020). This process occurs within the interfacial layer among the adsorbent and adsorbate. Adsorption is typically divided to two categories which are physisorption and chemical adsorption or chemisorption. In the case of physisorption, or physical adsorption, the interaction between the adsorbate and the adsorbent surface is characterised by the presence of weak Van der Waals forces, which serve to hold the former in place. In contrast, chemisorption, or chemical adsorption, involves the formation of strong chemical bonds between the adsorbate and adsorbent (Alaqarbeh et al., 2021; Lashaki et al., 2012; Sazali et al., 2020).

The efficiency of the process of adsorption is influenced by the solubility of adsorbate, whereby substances with a lower solubility in water are more readily removed. Furthermore, the effectiveness of the adsorption process is affected by the adsorbate's initial concentration. At higher concentrations, the initial mass transfer gradient is stronger, thereby driving the adsorption process (Abdel-Hady et al., 2023; Li, Liu, et al., 2020). The period of time that the adsorbent and adsorbate are in contact determines the equilibrium state of the adsorption process.

The temperature has a significant impact on the adsorption capacity. An endothermic process is indicated through an increase in adsorption capacity with higher temperature, whereby the adsorbate requires additional energy to bind effectively to the adsorbent's active sites. Conversely, the process is exothermic when the adsorption capacity decreases as the temperature rises because high temperatures destroy the bonds between the adsorbent and the adsorbate (Budnyak et al., 2020; Malbenia John et al., 2024).

The solution pH is also a great consequence, affecting adsorption efficiency by modifying the distribution of positive and negative charges that exist in the solution (Ali et al., 2020). The influence of these charges on the dissociation of functional groups on the adsorbent surface affects the process through mechanisms such as surface hydroxylation, acid-base dissociation and surface complex formation (Abegunde et al., 2020; Sudrajat et al., 2021).

2.4.1 Adsorption by carbon-based materials

The utilisation of solid materials as adsorbents is predicated upon their capacity to provide surfaces that facilitate the adsorption of a range of compounds. In recent years, there has been a notable increase in interest in carbon-based materials as adsorbents, driven by

their distinctive structural properties and the expanding applications across chemistry, physics, and engineering (Sabzehmeidani et al., 2021). These carbon-based structures, celebrated for their diversity and functionality, have proven to be effective in adsorbing a variety of water contaminants, such as metalloids, medications, pesticides, toxic metal ions, and other organic and inorganic substances (Akhtar et al., 2024). The versatility of carbon as an element is evidenced by its strength and its remarkable ability to form bonds with numerous other elements, which underpin its prominence in various fields (Thines et al., 2017).

The most commonly utilised carbon-based adsorbents derived from biomass include commercial activated carbons, graphene, graphene oxide and carbon nanotubes (Isaeva et al., 2021). The adsorption effectiveness of these materials is depending on the features of the adsorbate (including size, polarity, molecular weight, pKa, and functionality), the properties of the adsorbent (pore size, structure, and functional groups,) and solution parameters (including pH, temperature, and ionic strength) (Sabzehmeidani et al., 2021). The forces like van der Waals, dipole-dipole, hydrogen bonding, and dipole are essential for the binding and buildup for chemical substances on different adsorbents in the liquid phase. Among these interactions, $\pi - \pi$ stacking, hydrogen bonding, along with covalent, electrostatic forces, and the hydrophobic interactions, are of particular significance for effective adsorption (Dehgani et al., 2020).

2.5 Carbon-based material

Carbon-based materials are regarded as low cost and environmentally sustainable options that continue to attract significant interest due to their exceptional properties, including high electrical conductivity, rapid charge transfer capability, high stability and

ease of structural modification (Khan, 2021; Zhang et al., 2019). Despite the fundamental nature of carbon, researchers have sought to enhance its morphological characteristics and strategically modify its chemical composition with the objective of optimising performance (Cho & Lee, 2020). While modifications the morphology of carbon, which are usually made to increase pore size and surface area, generate an amorphous material, its chemical structure can undergo transformations through the application of both physical and chemical modification techniques (Ali et al., 2019; El-Hossary et al., 2021). Research has shown that the addition of functional groups markedly enhances both physical and chemical properties of the carbon, rendering it more versatile and applicable to advanced technologies (Cheng et al., 2022; Speranza, 2019). Up until now, numerous investigations have been conducted into the modification of carbon material, resulting in the discovery of new possibilities for optimised applications.

2.5.1 Plant derived carbon-based materials

In the natural environment, the term “biomass” is used to describe organic materials derived from animals, plants and daily waste. These materials are notable for their abundance of essential elements which include nitrogen, oxygen, hydrogen, and carbon (Soffian et al., 2022). Recently, there has been a notable interest in research interest in natural biomass because of its sustainable, carbon-rich resource used for synthesising carbon-based materials. This interest is derived from the accessibility, low-cost, environmentally friendly characteristics, unique nanoporous structure with large surface area, a wide-ranging of morphologies, and mechanical stability of the material (George et al., 2024; He et al., 2023). The specific microstructures and elemental compositions of carbon materials produced from biomass exhibit considerable variation depending on the original source of biomass used.

The most commonly employed precursor is plant-derived biomass, the chemical composition of which differs significantly across species and the parts. The majority of this group comprises lignin, hemicellulose, and cellulose, each of which possesses distinctive structural and chemical characteristics. Therefore, cellulose, the chemical constituents and structure of lignin, and hemicellulose are depicted in Figure 2.6. For example, analysis of dried coconut coir has revealed the presence of 46.48% lignin by weight, while cellulose and hemicellulose were found to comprise only 21.46% and 12.36%, respectively (Arsène et al., 2013). In contrast, dried hemp is composed of 67% cellulose, with lignin representing a mere 3.3% of its total weight (Reed & Williams, 2004). Similarly, Scots pine branches and stumps are characterised by substantial hemicellulose contents of approximately 32% and 28%, respectively, (Juha Nurmi, 1997; Liu et al., 2018; Tommi Raisanen & Dimitris Athanassiadis, 2013). Table 2.3 presents a thorough summary of the main chemical compositions of the different plant-based biomass sources.

Lignin has been determined to be the most stable of the aforementioned groups during thermal breakdown, which makes a substantial contribution to the final carbon yield. Furthermore, studies have shown that the cellulose and lignin interact at 550 °C. This indicates that a high lignin content, in conjunction with a low cellulose content, enhances properties such as conductivity, controlled defect formation, and graphitisation. Consequently, it renders the material highly suitable for environmental remediation (Cagnon et al., 2009; Thomas et al., 2019; Zhang et al., 2015).

Furthermore, dry flowers contain a range of organic compounds, including saccharides, glucosides, vitamins, and proteins. In a successful experiment, Wei et al. (2016) employed camellia petals as a carbon precursor with ammonium persulfate as a dopant,

producing S/N co-doped porous carbon nanosheets that had an exceptionally high BET surface area exceeding $1122\text{m}^2\text{g}^{-1}$. Chang et al., (2015) employed paulownia flowers, a commonly cultivated tree species in China, to synthesis nanostructured carbon materials that exhibit a distinctive porous texture and are enriched with various organic compound. Leaves exhibit the highest levels of saccharides and proteins among the various plant organs, along with the surface functional groups determined by the nitrogen and oxygen. Zhu et al. (2018) further developed this work by synthesising three distinct type of carbon materials from dead ginkgo leaves, employing a two-step process involving pyrolysis and subsequent activation by KOH, ZnCl_2 , and H_3BO_3 .

In 2019, a research team lead by authors successfully transformed discarded bamboo leaves, a common waster product, into a carbon-copper oxide nanocomposite with distinctive hierarchical structures (Wang et al., 2019).

Other than typical plant-derived such as seeds as it due to their tubular morphology with hollow and thin walls, are also considered to be promising precursor designed for the making of active carbon. For instance, Su et al. (2017) transformed poplar catkin biowaste into a hollow, hierarchically porous activated carbon nano mesh with an impressive BET surface area of $1893.0\text{m}^2\text{g}^{-1}$ and a total pore volume of $1.495\text{cm}^3\text{g}^{-1}$. Similarly, fruit peels, which are plentiful as waste and typically disposed of through incineration, present environmental challenges. However, they are rich is fibres and saccharides, making them ideal for the production of activated carbon. Yang & Park (2018) demonstrated this by synthesising MnO_2 /biomass-derived porous carbon (BPC) composites from dried banana peels, which preserved the peel's natural porous structure and facilitated MnO_2 growth without particle agglomeration. Furthermore, peanut shells have been employed to produce

stacked porous carbon compounds via a significant BET surface area of $1549\text{ m}^2\text{g}^{-1}$ (Xiao et al., 2018).

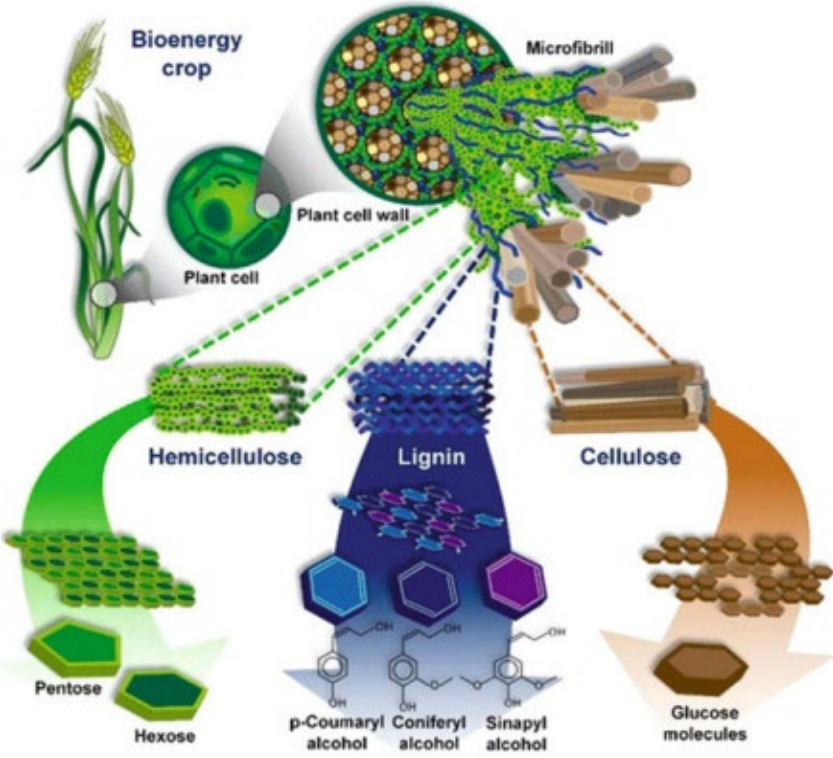


Figure 2.6: Structure of lignocellulosic biomass containing lignin, cellulose, and hemicellulose (Singh et al., 2022)

Table 2.3: The main chemical compositions of various plant-based biomass sources (on a dry weight% basis)

Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Referecnes
Corn stalks	35 – 37	24 – 26	18 – 20	(Ioelovich & Ioelovich, 2013)

Table 2.3: continued

Corn cobs	34 – 36	36 – 38	9 – 11	(Ioelovich & Ioelovich, 2013)
Corn stover	35 – 37	28 – 30	18 – 20	
Wheat straw	34 – 36	28 – 30	15 – 17	
Rice straw	34 – 36	25 – 27	7 – 9	
Barley straw	33 – 40	20 – 35	8 – 17	(Biswas et al., 2015)
Switch grass	36 – 38	26 – 28	17 – 19	(Ioelovich & Ioelovich, 2013)
Scots pine branches	32.0	32.0	21.5	(Tommi Raisanen & Dimitris Athanassiadis, 2013)
Scots pine bark	22.0	8.1	13.1	
Scots pine stem wood	40.7	26.9	27.0	
Scots pine roots	28.6	18.9	29.8	(Liu et al., 2018)
Scots pine stumps	36.4	28.2	19.5	

Table 2.3: continued

Sunflower seed hulls	30.0	38.5	26.4	(De’Nobili et al., 2021)
Willow leaves	18.5	14.7	20.0	(Chauvet, 1987)
Poplar leaves	22.3	12.8	23.2	
Coconut coir	21.46	12.36	46.48	(Arsène et al., 2013)
Banana leaves	25.65	17.04	24.84	
Hemp	67.0	-	3.3	(Reed & Williams, 2004)

2.6 Graphene

Graphene is an incredible carbon nanomaterial made up of two-dimensional layers that consist of single-atom thick sheets of sp^2 -bonded carbon atoms, all neatly arranged in a honeycomb lattice structure (Choi et al., 2010; Huang et al., 2015). Its structure bears similarity to that of benzene rings, wherein hydrogen atoms are swapped out for the carbon atoms, which gives it a naturally hydrophobic quality because it lacks oxygen containing functional groups (Dasari Shareena et al., 2018). In addition, graphene is a carbon allotrope with a planar of sp^2 -bonded atoms with a molecular bond length of 0.142 nm. The stacking of these layers’ yields graphite, characterized by its interplanar distance of 0.335 nm (Sharon & Sharon, 2016).

The excellent properties of graphene have drawn substantial interest, specifically its high theoretical specific surface area of $2630\text{ m}^2\text{g}^{-1}$ (Zhu et al., 2010), and its high intrinsic

mobility of $200,000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (Bolotin et al., 2008; Morozov et al., 2008), a high Young's modulus of approximately 1.0 TPa (Lee et al., 2008), and an impressive thermal conductivity of about $5000 \text{ Wm}^{-1} \text{K}^{-1}$ (Balandin et al., 2008). Additionally, graphene has high optical transmittance ($\sim 97.7\%$), high electrical conductivity, and the ability to withstand a current density of 108 A/cm^2 (Moser et al., 2007).

Moreover, graphene acts as a semimetal with a distinctive benzene ring-like electronic structure comprises of six π - orbitals with three occupied bonding and three unoccupied antibonding orbitals, with a small bandgap separating them. This arrangement results in a small overlap between the valence and conduction bands, thus facilitating the efficient transport of electrons from the valence band to the conduction band without much generation of heat (Rao et al., 2009; Zhen & Zhu, 2017). The effective surface area of graphene has specific correlation with the degree of layer agglomeration, thus reducing the effective surface area available for different applications. Notably, functionalization of pure graphene by introducing other compounds has been shown to prevent agglomeration and enhance surface area (Lü et al., 2012). Graphene has attracted considerable attention from the scientific community in recent years, due to its remarkable electronic, optical, magnetic, thermal, and mechanical properties, as well as its large surface area (Bhuyan et al., 2016). The excellent properties of graphene continue to promote creative developments and enhance its potential applications in various scientific and technology disciplines.

2.6.1 Graphitization and catalytic graphitization of biomass waste materials

The process of graphitization represents a transformative change whereby amorphous carbon is converted into a more structured, graphitic form. This process typically involves prolonged heat treatment, during which thermal energy facilitates the

rearrangement of carbon atoms into a crystalline lattice that is characteristic of graphitic carbon. The conventional industrial methods for synthesising graphite from fossil-based raw materials required temperatures of extreme graphitisation, often reaching up to 3000 °C (Haluska et al., 2023). However, an alternative approach is the production of artificial graphite using biomass derived carbon precursors, such as biochar and activated carbon (Destyorini, Irmawati et al., 2021a; Sun et al., 2022; Weldekidan et al., 2022). This approach not only exploits the plentiful and cost-effective nature of biomass but also reduces the requisite graphitisation temperatures, thereby conferring substantial environmental benefits.

A number of graphitisation methods have been developed, including direct heat treatment, catalytic graphitisation and the addition of activating agent (Yap et al., 2023). Of these methods, catalytic graphitisation has attracted considerable interest due to its capacity to reduce the requisite temperature to (800 – 1300 °C) and enhance the degree of graphitisation. (Barnakov et al., 2015; Destyorini, Irmawati, et al., 2021b; Neeli & Ramsum, 2018; Thompson et al., 2015). This process encompasses both physical and chemical transformations, which are facilitated by catalysts. These catalysts are typically transition metals, including iron, nickel, and cobalt. They reduce the activation energy needed for the conversion of amorphous carbon into crystalline graphite (Nuriskasari et al., 2024).

Generally, two principal mechanisms are responsible for the process of catalytic graphitisation. The initial process entails the dissolution of carbon atoms into catalysts, which is then followed by their precipitation as graphitic material. The second mechanism involves the formation of carbide intermediates, which subsequently decompose into graphitic carbon (Destyorini, Yudianti, et al., 2021; Hunter et al., 2022; Li, Zhang, et al., 2020). These mechanisms illustrate the dynamic interplay between catalysts and carbon

precursors, offering a pathway to efficiently produce high-crystalline graphite at relatively lower temperatures. This advancement highlights the potential of catalytic graphitisation as a more sustainable and scalable approach to graphite synthesis, particularly when employing renewable biomass feed stocks.

2.7 Graphene oxide

Graphene oxide (GO) can be defined as multi-layered carbon nanomaterial that is distinguished by the incorporation of oxygen-containing functional groups, including carbonyl ($=O$), hydroxyl ($-OH$), epoxy ($-O-$), and carboxyl ($-COOH$). These groups are distributed across both its basal planes and edges. Graphene oxide is synthesised through the oxidative treatment of graphite, whereby graphite oxide is produced and subsequently exfoliated to yield graphene oxide sheets. The specific characteristics of graphene oxide, including the type and density of oxygen functionalities, are highly sensitive to synthesis technique employed, which directly affects its overall properties (Jiříčková et al., 2022a).

The presence of oxygen-containing functional groups on the surface of graphene oxide renders it an ideal precursor for synthesis of plethora of graphene derivatives, including fluorographene, bromographene, and reduce graphene forms. The reduction of graphene oxide, either thermally or chemically, yields reduced graphene oxide (RGO), thereby providing further opportunities for the tailoring of its structure and properties for specialised applications, as illustrated in Figure 2.7 (Jiříčková et al., 2022a). Interestingly, recent research has demonstrated the potential of graphene oxide (GO) for advanced technological applications in fields ranging from solar cells and hydrogen storage to transparent conductive films, polymer composite, biomedicine, nanoelectronic devices, energy storage, biosensors, catalysis and transparent electrodes (Kumar Patel Amar

Veerangana Rani et al., 2016; Silva et al., 2024). Furthermore, the presence of oxygen functionalities increases the interlayer spacing in graphene oxide, enhancing its specific surface area, improving mesoporosity, and imparting a certain level of electrical conductivity (Nikam et al., 2024).

The graphene oxide (GO) can be synthesised through three primary methods: Hummers method, Brodie method, and Staudenmaier method. All of the aforementioned methods employ graphite as the raw material, subjecting it to various strong oxidants in order to yield graphene oxide sheets. Of these, the Hummers method has gained widespread acceptance due to its shorter reaction time, higher efficiency, and improved safety, making it promising approach for industrial-scale production of graphene oxide (GO) (Chen et al., 2022; Omar et al., 2022). Comparative analyses by Boehm and Scholz who identify the advantages and limitations of each technique. They note that the Hummer method produces graphene oxide with a higher O/C ratio (approximately 47% carbon content), which is advantageous for certain applications (Trikkaliotis et al., 2021). Furthermore, Hummers method exhibited a lower deflagration point compared to Staudenmaier and Brodie methods in the synthesis of graphene oxide. In Hummers method, graphite undergoes oxidation using a combination of strong acids, including nitric acid and sulfuric acid, in conjunction with potassium permanganate, leading to a highly efficient conversion with robust oxidation (Chen et al., 2022).

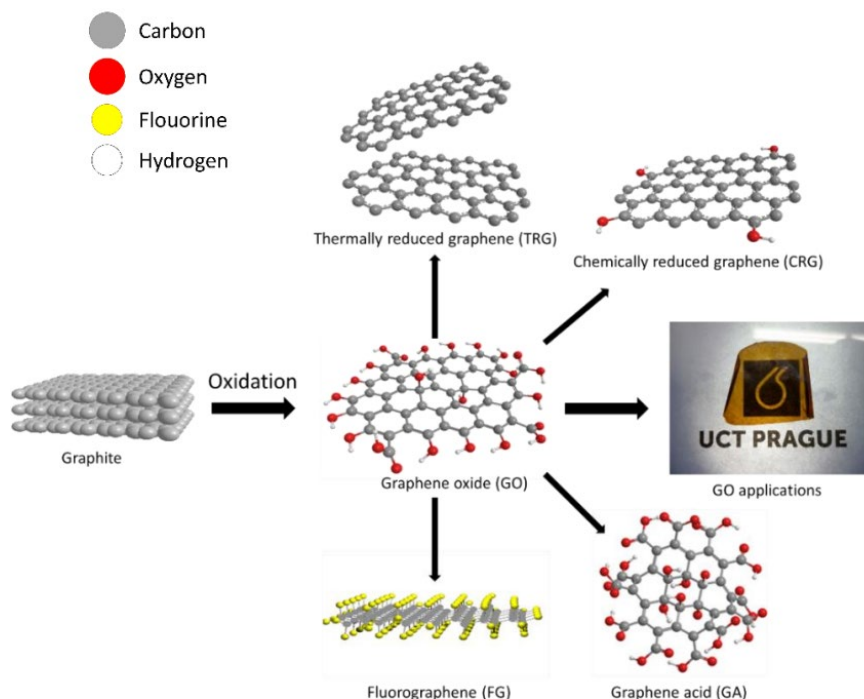


Figure 2.7: Scheme of preparation and utilization of graphene oxide (Colours of atoms: grey - carbon, red - oxygen, yellow - fluorine, white - hydrogen) (Jiříčková et al., 2022a).

2.8 Oxidation method of carbon-based material

In recent years, there's been a surge of both theoretically and experimental research aimed at unravelling the structure of graphite oxide (GO), especially since it plays a crucial role as a precursor in creating graphene-based materials. Understanding the structure makeup of graphene oxide is essential for preparing GO, and this understanding deeply tied to structural analysis. Typically, GO is produced by the intercalating and oxidizing graphite powder, a key process for generating GO in large quantities using various well-established methods. The history of GO synthesis is particularly intriguing, especially GO has evolved and improved over time.

The most commonly used methods for synthesizing graphite oxide include the Brodie method developed by Benjamin Collins Brodie, 1859, the Staudenmaier method, the

Hofmann method and the Hummers method (Hummers & Offeman, 1958) along with their modified versions that aim to boost efficiency and yield (Trikkaliotis et al., 2021).

These methods typically involve a chemical reaction between graphite powder and strong acids like hydrochloric acids (HCl), sulfuric acid (H_2SO_4) and nitric acid (HNO_3). After this acidic treatment, alkali metals or their compounds, such as potassium chlorate ($KClO_3$), potassium permanganate ($KMnO_4$), and sodium nitrate ($NaNO_3$), are intercalated into graphitic layers. This intercalation process greatly aids in exfoliating the graphitic layers, breaking them down into smaller pieces and enhancing the overall oxidation process (Singh et al., 2016).

Researchers are trying to improve graphene oxide (GO) by making it more efficient, increasing its production, and enhancing its quality. There is a lot of interest in GO because it is essential for making graphene, which has many potential uses in science and technology fields.

2.8.1 Brodie's oxidation method

In 1859, Benjamin Collins Brodie, 1859 created a new method to oxidize graphite. He used potassium chlorate ($KClO_3$) and fuming nitric acid (HNO_3). By applying these chemicals to graphite powder, he made a new substance containing carbon, oxygen and hydrogen. This process increased in the weight of the graphite. He was able to get this new material in crystal form, but measuring the angles of the crystal lattice were difficult. Repeated treatments added more oxygen was 61.04: 1.85: 37.11 matching the formula $C_4H_{11}O_5$. These materials mixed well in plain or basic water but not in acidic conditions, so Brodie named it "graphic acid". When heated to 220°C, the material changed its elemental balance to 80.13: 0.58: 19.29 (C: H: O) because it released gases like carbonic

acid and carbonic oxide. Although Brodie's method was important for making graphite oxide, it had issues. The process took a long time, produced dangerous gases, and could explode due to potassium chlorate($KClO_3$), making it risky for large production. Despite these problems, Brodie's work was vital in advancing the creation and study of graphite oxide, making an important step in the evolution of carbon-based materials.

2.8.2 Staudenmaier method

Staudenmaier built upon Brodie's work from 1898 to increase the production of graphite oxide (GO) and make the process safer. In the study, a key change by using a mix of sulfuric acid (H_2SO_4) and nitric acid (HNO_3) as the oxidizers, replacing the dangerous fuming nitric acid that Brodie initially used. The method involved oxidizing graphite slurry in one step. This was done by mixing sulfuric acid and nitric acid, and then slowly adding potassium chlorate ($KClO_3$) over several stages. The reaction took place at about 90°C and needed four days to complete. Despite taking a long time, this approach successfully produced graphite oxide with a carbon to oxygen ratio similar to Brodie's method.

This improved technique was named the Staudenmaier-Hoffman-Hamdi method (SHHM), as reported by Sagadevan et al., 2017. While the SHHM's one-step process made the reaction more efficient, it was still time-consuming and required high temperatures. Furthermore, the use of potassium chlorate still posed risks of explosions, raising safety concerns. Even with these challenges, Staudenmaier's work marked an important advance in the synthesis of graphite oxide and laid the groundwork for further research in carbon-based materials.

2.8.3 Hofmann method

In 1937, Hofmann improved the process of making graphite oxide. In the process, a mix of high concentrated sulfuric acid(H_2SO_4), high concentrated nitric acid(HNO_3), and potassium chlorate($KClO_3$). Potassium chlorate acts as a strong oxidizing agent. It helps to oxidize graphite powder in acidic solution effectively and provides dioxygen needed for the oxidation process. Hofmann's method is widely used by researchers to synthesize graphite oxide for different applications (Poh et al., 2013; Rezaei & Saghazadeh, 2017; Singh et al., 2016). Although the method is effective, it involves safety risks due to the use of potassium chlorate, which can be explosive if not handled carefully. Despite these risks, this method remains a key approach in making graphite oxide. It continues to be an important foundation for advancements in materials made from graphene.

2.8.4 Hummers method

In 1958, a new method was introduced a groundbreaking way to create graphite oxide was developed by Hummers and Offeman. Potassium permanganate(K_2MnO_4), along with graphite, sulfuric acid(H_2SO_4), and sodium nitrate($NaNO_3$). This new method made a big difference in producing graphene oxide (GO), as it resulted in a highly oxidized and well-organized structure that mixes easily with water Hummers & Offeman, (1958). The Hummers method stands out from older techniques for several reasons related to forming graphite oxide. The process was safer because it naturally created nitric acid, avoiding the need for dangerous, strong acids. Also, switching from another chemical to potassium permanganate reduced harmful gas emissions, making the process more environmentally friendly and safer. However, this method has some issues. It still releases some harmful gases like nitrogen oxide during the process. There are also worries about the contamination of heavy metals. Additionally, sodium and nitrate ions in the final product are hard to

remove. A major safety concern is the risk of explosion if manganese heptoxide forms when potassium permanganate reacts with concentrated sulfuric acid at temperatures over 55°C (Shamaila et al., 2016). Despite these challenges, the Hummers method is still widely used for producing graphene oxide because it provides a dependable and scalable approach for many applications.

2.8.5 Tour's method

The Tour method was created by Professor James Tour and his team at Rice University, was a better way to synthesize graphene oxide (GO) from graphite through chemical exfoliation. (Magne et al., 2022; Shamaila et al., 2016). This method involves the chemical exfoliation of graphite to obtain GO sheets (Jiříčková et al., 2022). This process starts by oxidizing graphite with high concentrated sulfuric acid (H_2SO_4) and nitric acid (HNO_3). These chemicals help to oxidize graphite smaller pieces, and more steps follow to make high-quality GO. This GO can be used in many applications (Jiříčková et al., 2022). One of the distinguishing features of the Tour method is that it employs a plasma torch to help add oxygen-containing functional groups to the graphite structure. This produces GO with higher graphitization level and lower concentration of oxygen containing functional groups compared to GO synthesized using the Hummers method. This gives it better structural integrity and functionality. Though it has the benefit of producing graphene oxide (GO) with the desired characteristics, the Tour method has its limitations. Typically, this method is accompanied by a cost increase and the need for specialized equipment, which may restrict its scalability and more extensive use in industrial-scale production (Jiříčková et al., 2022). Nonetheless, the process is an important advancement in graphene oxide synthesis with the offering of a solid avenue for high-quality GO synthesis with meticulous control over its structural and chemical characteristics.

2.8.6 Modified Hummers method

In 2013, the author proposed a revised form of the Hummers method that uses a refined and efficient strategy that ensures sustainability and reduces ecological costs (Chen et al., 2013). This improved strategy entails oxidation of graphite by using potassium permanganate ($KMnO_4$) in high concentrated sulfuric acid (H_2SO_4) under a lowered temperature. Adding water and hydrogen peroxide (H_2O_2) to the reactant mixture allows for direct extraction of sodium nitrate from this mixture and hence makes it more environmentally friendly. The chemical properties and structural of the resulting graphene oxide (GO) are similar to those obtained using traditional Hummers method while minimizing reagent amount used in process. Therefore, this method is more financially feasible and environmentally friendly strategy.

In consideration of these developments, Peng et al. (2015) introduced a dramatically improved and sustainable methodology using an iron-based oxidant. This method has several key advantages as it excludes heavy metal ions and toxic gas byproduct formation, avoid explosion risks, and operates under moderate conditions without requiring thermal control. In addition, it allows for easy scalability of reactants to achieve optimal yields with lowered costs and environmental impact. This advancement represents continued strides toward more environmentally benign and financially efficient methods for producing quality graphene oxide.

Table 2.4: The comparison of oxidation graphene of synthesis methods

Method	Oxidants	Solvent	Pros	Cons
Brodie	$KClO_3$	HNO_3	-	Time consuming process Produced toxic gases Risk of explosion
Staudenmaier	$KClO_3$	$HNO_3 + H_2SO_4$	Removing fuming nitric acid	Time consuming High temperature Risk of explosion
Hofmann	$KClO_3$	$H_2SO_4 + HNO_3$	-	Risk of explosion
Hummers	$KMnO_4 + NaNO_3$	H_2SO_4	Highly oxidized and well-organized structure Reduce harmful gas emissions	Harmful gas: nitrogen dioxide Contamination of heavy metals Risk of explosion

Table 2.4 continued

Tour	$KMnO_4$	$H_2SO_4 + HNO_3$	High quality of graphene oxide with desired characteristics	Expensive Need for specialized equipment
Modified Hummers	$KMnO_4$	H_2SO_4	Cheaper and environmentally friendly	-

2.9 Application of graphene oxide in wastewater treatment

Water pollution is a massive environmental issue that is caused by human activities in a variety of ways. It has a negative impact on human health, increases disease rates, and causes the demise of aquatic life, land animals, and plants. Poisonous gases, pesticides, harmful chemicals, heavy metals, crude oil, dyes, and a host of other substances that cause extremely dangerous to humans, animals, and plants are just a few examples of these pollutants. In order to counteract this, many researchers are still looking into effective ways to detoxify our polluted environment, which is replete with these dangerous substances. Chemical reduction, biological treatment, adsorption, photocatalytic degradation, physical

removal of pollutants, and adsorption are a few of the techniques used to remove these pollutants (Jiříčková et al., 2022a; Singh et al., 2023).

Graphene oxide and its derivatives possess immense potential as materials for environmental detoxification, especially in wastewater treatment applications. These outstanding substances can enhance the effectiveness of several conventional methods employed for environmental detoxification purposes. Adsorption stands out as a prominent approach for harnessing the unique properties of graphene oxide in ecological applications. In this regard, numerous researchers have demonstrated significant advancements in adsorption utilizing graphene oxide and its derivatives-based materials, contributing to this field's latest development (Kumar et al., 2023).

Adsorption is a versatile technique that can use physical or chemical interactions to remove inorganic or organic pollutants. Various adsorbents are currently employed in wastewater treatment, including activated carbon, starch, agricultural waste, cyclodextrins, and zeolite. However, graphene oxide a novel material exhibits great promise in the field of adsorption for environmental applications, particularly in wastewater treatment. Graphene oxide possesses remarkable characteristics that contribute to its high adsorption capacity. These include a large theoretical surface area, substantial porosity, abundant oxygen-containing functional groups, high hydrophilicity, and $\pi - \pi$ bonding. These features enable graphene oxide to effectively capture and bind contaminants. The process of adsorption can take place via both chemical and physical mechanisms, depending on the specific interactions involved. The Langmuir, Freundlich and Temkin models are utilized to determine the adsorption isotherms and their behaviour. These isotherms provide valuable insights into the adsorption capacity, surface coverage, and equilibrium conditions, allowing

for a significant comprehension of the process of adsorption on the surface of graphene oxide. In general, due to its remarkable properties and ability to adsorb contaminants, graphene oxide has a high adsorption capacity which makes it a viable candidate for use as an adsorbent in wastewater treatment research. Active studies focus on investigating the potential of graphene oxide for efficient and sustainable environmental solutions (Allgayer et al., 2020; Kim et al., 2018; Kumar et al., 2023; Kyzas et al., 2014). Graphene oxide has shown exceptional adsorptive properties for the removal of different types of heavy metals. According to Azam et al. (2022), lead (Pb) removal from water using graphene oxide was treated with waste dry cell batteries and achieved an astounding retention rate of 98.87% within twenty minutes. The Langmuir isotherm model is a commonly used model in electrochemistry to describe the adsorption of species (such as ions, molecules, or atoms) onto a solid surface, provided a good fit, with a calculated maximum adsorption capacity of 55.80 mg g^{-1} . Moreover, graphene oxide material showed the ability to be regenerated and maintained a 90% removal efficiency for lead (Pb) even after six successive cycles. In another study by Lingamdinne et al. (2016), it was found that 1.0 g/L graphene oxide displayed a maximum adsorption capacity of 21.8 mg/g for removing Co (II) ions at pH 5.5 and 298 K. Similarly, White et al. (2018) reported that graphene oxide synthesized using a modified Hummer's method exhibited a high removal efficiency of copper (II) ions (Cu^{2+}) from aqueous solutions, reaching 97% at pH 6 and 298K. The value for maximal adsorption capacity was determined to be 277.77 mg/g for graphene oxide (GO). Furthermore, graphene oxide demonstrated effectiveness in removing hexavalent chromium Cr (VI). A study by Mondal & Chakraborty (2020) indicates that graphene oxide achieved a maximum removal percentage of 92.8% under acidic conditions which is pH 4. It was found that the adsorption process obeyed the Langmuir isotherm adsorption model, which yielded the maximum

adsorption capacity of $1.222\mu\text{g}/\text{g}$. Furthermore, Farag et al. (2022) demonstrated that the modified Hummers method of graphene oxide synthesis has shown a high degree of efficiency in removing lead ions (Pb^{2+}) and aluminium ions (Al^{3+}) at pH 6 and room temperature. The removal rates reached 92.6% and 91.9% respectively, after 4 hours of treatment. These findings highlight the significant adsorption capabilities of graphene oxide towards heavy metal ions and its potential for effective environmental remediation applications.

Additionally, graphene oxide showcases remarkable promise in water purification processes, including the removal of various toxic contaminants, such as dyes. It has been noted that graphene oxide demonstrates remarkable adsorption capacities for particular dyes, like Methylene Blue and Rhodamine B. Notably, Mao et al. (2020) discovered that the maximum capacities of adsorption for Methylene Blue and Rhodamine B were 403.3 mg/g and 686.6 mg/g, respectively, exhibited by graphene oxide. The kinetic study conducted in this research confirmed the suitability of the pseudo-second-order kinetic model and Langmuir model for describing the adsorption process. In the investigation by Molla et al. (2019), it was observed that graphene oxide exhibited rapid and quantitative selectivity for positive dyes, such as Methylene Blue and Rhodamine B. Within a short span of 15 minutes, impressive removal efficiencies of 97% for Methylene Blue and 88% for Rhodamine B were achieved. Conversely, the negative dye, methyl orange, did not exhibit significant adsorption. According to Mahich et al. (2022), at a temperature of $150\text{ }^{\circ}\text{C}$, Graphene Oxide can remove 95% of Methylene Blue dye with the help of 10 mg of sample powder in a 50-ppm solution over a 4-hour period. Moreover, Yang et al. (2022) highlighted that a small amount of graphene oxide, specifically 0.24g, achieved an impressive removal rate of 92.55% for Rhodamine B within just 23 minutes. It is noted that adsorption was achieved

following the pseudo-second-order model. Also, the Langmuir-Freundlich isotherm provided the best fit with the equilibrium data in this case, which showed the maximum adsorption capacity of 107.230 mg/g. These findings underscore the exceptional adsorption capabilities of graphene oxide to effectively eliminate dyes from wastewater, tailoring it as a highly effective adsorbent for use in the treatment of water resources.

2.10 Adsorption on methylene blue by different carbon-based materials

The carbon adsorption process can be categorized into four distinct groups as delineated by (Santoso et al. 2020): superior adsorbents exhibiting an adsorption capacity exceeding 1000 mg/g, excellent adsorbent demonstrating an adsorption capacity ranging from 500 to 1000 mg/g, moderate adsorbent which are possessing an adsorption capacity of 100 to 500 mg/g and poor adsorbents characterized by an adsorption capacity of less than 100 mg/g. The adsorption capacity of activated carbon derived from *Ficus carica* bast (FCBAC) was determined to be 47.62 mg/g, as reported by Pathania et al. in 2017. The adsorption capacity of activated carbon derived from mandarin orange peels (AC – MOP) was 74.15 mg/g, as reported by Thabede (2023). The adsorption capacity of biochar, produced through the slow pyrolysis of a fallen leaf of *Magnolia Grandiflora* L, was found to be 101.27 mg/g (Ji et al., 2019). The adsorption capacity of modified biochar (g- C_3N_4) derived from straw and urea was found to be 833.75 mg/g (Li, 2019). The adsorption capacity of the green biochar/iron oxide composite was found to be 862 mg/g (Zhang et al., 2020). The adsorption capacity of chitosan-derived three-dimensional porous carbon derived from chitosan was found 925.93 mg/g (Jin et al., 2018). The adsorption capacity of the carbon nanotubes was determined to be 1189 mg/g (Wang et al., 2018).

2.11 Kinetic study

The adsorption kinetics have been shown to be a two-steps sequential process in previous studies. At first, the adsorbate moves from the bulk solution towards the surface of the adsorbent. Subsequently, adsorbable diffuses further, becoming organised within the sorbent's internal pore structure. This step is important in analysing the mechanism as a whole due to its rate-limiting nature. Therefore, the kinetics of the adsorption reaction models must be tailored to the described mechanism by properly applying diffusion-centred adsorption models (Alaqarbeh, 2021). Table 2.5 provides details on both the linear and non-linear representations of the kinetic models.

2.11.1 Pseudo-first-order model

The pseudo-first-order model is a widely used analytical tool for the interpretation of adsorption data pertaining to adsorbates extracted from aqueous solutions. This model describes how the adsorption rate is directly dependent on the number of vacant binding sites on the adsorbent surface. The kinetics of this process are generally represented concluded the following equation (Ebelegi et al., 2020).

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right) k \quad \text{Equation 2.1}$$

2.11.2 Pseudo-second-order model

The pseudo-second-order kinetic model assists in the comprehensive understanding of the rate and dynamics of adsorption of an adsorbate onto an adsorbent. The functional groups that are present on the surface of the adsorbent have a significant impact on the adsorbate. Therefore, the chemical bonding interactions are paramount to be considered while determining the adsorption capacity of the adsorbent. This model values the

equilibrium adsorption and thus it depends upon the amount of adsorbate that gets adsorbed at the equilibrium level. Hence, it helps us understand the rate of the sorption process and also to know the limits of sorption capacity. For clarification, below is presented the linearised form of the above expression (Ebelegi et al., 2020).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{Equation 2.2}$$

Table 2.5: The kinetic models in non-linear and linear forms

Model	Equation	Plots
Pseudo-first-order		
Non-linear form	$Q_t = Q_e(1 - e^{-k_1 t})$	$Q_t \text{ VS } t$
Linear form	$\log(Q_e - Q_t)$ $= \log Q_e - \left(\frac{k_1}{2.303}\right) t$	$\log(Q_e - Q_t) \text{ VS } t$
Pseudo-second-order		
Non-linear form	$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t}$	$Q_t \text{ VS } t$
Linear form	$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$	$\frac{t}{Q_t} \text{ VS } t$

2.12 Adsorption isotherm

An adsorption isotherm assists in studying the dynamics of an adsorption system and evaluated the efficiency of the relationship between adsorbent and adsorbate. The capacity of the carbon-based material synthesized from coconut husk to adsorb methylene blue was evaluated by analyzing the characteristics of adsorption isotherm plots. Equilibrium isotherm

data were fitted to Langmuir, Freundlich, and Temkin adsorption models in this investigation. The linear regression analyses were used to determine the model with the best fit. Table 2.6 summarizes the synthesis results of the various isotherm models, while Table 2.7 provides details on both the linear and non-linear representations of these models.

2.12.1 Langmuir Isotherm model

Langmuir isotherm emerged to model the interactions between gases and solid surfaces, but it is now finding application with diverse adsorbents (Elmorsi, 2011). This is an empirical model based on kinetic considerations where the rates of adsorption and desorption that serve as the basis for this model: (a) adsorption occurs in a monolayer, (b) uniform sites, (c) uniform adsorption energy, and (d) no lateral interactions between adsorbed molecules. Thus, the Langmuir isotherm can be expressed as: (Kalam et al., 2021):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{Equation 2.3}$$

Where q_m is the maximum amount of adsorbed surfactant in mg/g and K_L is the Langmuir constant in L/mg. The non-linearized version of equation (2.3) is

$$\frac{C_e}{q_e} = \frac{1}{K_L q_o} + \frac{C_e}{q_o} \quad \text{Equation 2.4}$$

When C_e/q_e is plotted against C_e , a straight line with a slope of $1/q_o$ and an intercept of $1/K_L q_o$ will be obtained. The linearized version of equation (2.4) is

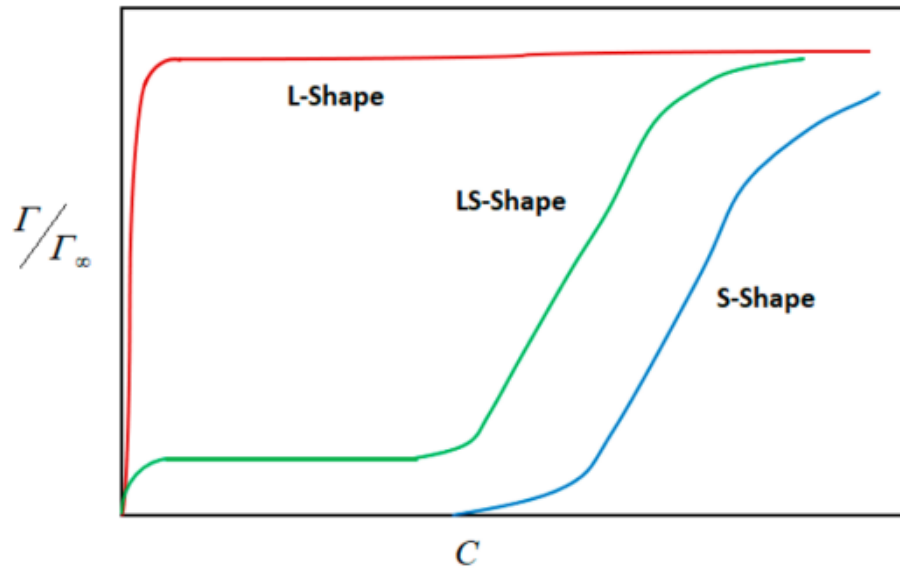


Figure 2.8: L-, S-, and LS-shape adsorption isotherm. Γ and Γ_∞ are adsorption and maximum adsorption, respectively, and C is the concentration (Kalam et al., 2021)

Adsorption isotherms are usually categorised into three distinct categories: L-shape (Langmuir), S-shape (S-type), and the LS-shape (double plateau), as illustrated in Figure 2.8. The L-shaped curve, which is frequently observed for dilute solutions at a solid/liquid interface, is well-described by the Langmuir model, which represents monolayer adsorption. In contrast, the S-shape curve distinguished by an initial shallow slope, followed by a rapid increase, which suggests a gradual activation process for adsorption. The LS-shaped curve, which is unique in its double plateaus structure, indicates a complex adsorption mechanism involving multiple stages (Kalam et al., 2021). The monolayer implies uniform adsorption sites where each site can accommodate only one molecule, which calls for identical adsorption sites. Once a surfactant molecule occupies a site, no further adsorption can occur. At very low concentrations ($K_L C_e \ll 1$), this model transitions to Henry's model. The Langmuir isotherm model, represented by the L-shaped curve in Figure 2.8, which has a single plateau. As noted by its description, the separation factor R_L is an equilibrium parameter that is a determining characteristic of the Langmuir model surfactant adsorption

isotherm and identifies the degree of adsorption preferentiality. (Gunawardene et al., 2021). This can be expressed mathematically as follows in equation (2.3):

$$R_L = \frac{1}{1 + K_L C_o} \quad \text{Equation 2.3}$$

Where K_L represents the Langmuir constant, and C_o stands for the maximum initial concentration of the surfactant. Technical term abbreviations will be explained upon first use. Generally, R_L value of less than 1 ($R_L < 1$), it signifies favorable adsorption, R_L value approximately equivalent to 0 ($R_L \sim 0$) point to irreversible adsorption, an R_L value of 1 ($R_L = 1$) implies a linear adsorption isotherm and an R_L value greater than 1 ($R_L > 1$) corresponds to unfavourable adsorption.

2.12.2 Freundlich Isotherm model

In contrast to the Langmuir isotherm, this empirical model addresses adsorption behaviour that involves several layers on sites with varied features. It operates under the assumption that the distribution of adsorption heat and the surface affinities across the surface of heterogenous are not uniform. The following equation can be utilised for showing the mathematical model (2.4):

$$\ln q_e = \ln b + \frac{1}{n} \ln C_e \quad \text{Equation 2.4}$$

A graph of the natural logarithm of the equilibrium constant, $\ln q_e$ versus the natural logarithm of the concentration, $\ln C_e$ result in a linear relationship, with a slope equal to 1 divided by the reaction order, $=1/n$ and an intercept equivalent to the natural logarithm of the pre-exponential factor, $\ln b$.

The linearized representation is simple and uncomplicated. However, this approach introduces errors that can lead to inaccurate parameter predictions. Consequently, it is advisable to employ nonlinear regression to determine the model parameters when dealing with the nonlinear Freundlich model (Wang & Guo, 2020).

Multilayer adsorption has been shown to be described by Freundlich isotherm, which implies an exponential decline in the energy distribution of adsorption sites. However, it is limited in its ability to be applied to a wide variety of adsorption data (Al-Ghouti & Da'ana, 2020).

2.12.3 Temkin Isotherm model

The Temkin model is based on the assumption of a multilayer adsorption process that considers the interaction between the adsorbate and adsorbent. However, it does not account for concentration values outside the right range, either too low or too high. The non-linear representation of the Temkin isotherm can be described as follows in equation (2.5):

$$q_e = \frac{RT}{b} \ln(K_m C_e) \quad \text{Equation 2.5}$$

Where R is the universal gas constant in J/ (mol K), T is the temperature in K, b is the Temkin constant related to sorption heat in J/ mol, and K_m is the Temkin isotherm constant in L/g.

The linearized form can be formulated as follows in equation (2.6):

$$q_e = \frac{RT}{b} \ln C_e + \frac{RT}{b} \ln K_m \quad \text{Equation 2.6}$$

Creating a graph of q_e against the natural logarithm, $\ln C_e$ will result in a linear relationship, with slope $= \frac{RT}{b}$ and intercept $= \frac{RT}{b} \ln K_m$.

As the surface coverage increases, the Temkin model assumes that the heat of adsorption of all molecules in the layer reduces linearly instead of logarithmically (Foo & Hameed, 2010).

Tables 2.6 and 2.7 provide an overview of the different model of isotherms, including both linear and non-linear forms.

Table 2.6: Summary of the different isotherm models

Adsorption isotherm	Axes		Slope	Intercept	Summary	References
	Ordinate	Abscissa				
Langmuir	C_e/q_e	C_e	$1/q_o$	$\frac{1}{K_L q_o}$	• Monolayer adsorption • Homogeneous solid surfaces	(Langmuir, 1916)
Freundlich	$\ln q_e$	$\ln C_e$	$1/n$	$\ln b$	• Ideal for adsorption throughout several layers • Suitable for heterogeneous surfaces • Not applicable to an extensive range of adsorption data •	(Foo & Hameed, 2010) (Al-Ghouti & Da'ana, 2020)

Table 2.6: continued

Temkin	q_e	$\ln C_e$	$\frac{RT}{b}$	$\frac{RT}{b} \ln K_m$	The heat of adsorption of all molecules in the layer decreases linearly rather than logarithmically as surface coverage growth.	(Foo & Hameed, 2010)
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Table 2.7: The isotherm models in non-linear and linear forms

Isotherm	Nonlinear form	Linear form	Plot
Langmuir	$q_e = \frac{K_L C_e}{1 + K_L C_e}$	$\frac{1}{q_e} = \left(\frac{1}{K_L q_m} \right) \frac{1}{C_e} + \left(\frac{1}{q_m} \right)$	$\frac{1}{q_e}$ VS. $\frac{1}{C_e}$
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$\log q_e$ VS. $\log C_e$
Temkin	$q_e = \frac{RT}{b} \ln(K_T C_e)$	$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	q_e VS. $\ln C_e$

2.13 Summary of literature review

The increasing sophistication of sustainable materials and environmental remediation techniques highlights the critical role of carbon-based adsorbents derived from agriculture by-products. In the light of the ongoing deterioration of the natural environment, particularly the contamination of water resources, cost-effective solutions are needed, renewable, and highly efficient adsorbents. A substantial body of research has demonstrated

that lignocellulosic biomass, such as coconut husk, represents a plentiful and valuable source for the production of high-performance adsorbents. The utilisation of techniques such as pyrolysis, chemical activation, and structural modification has led to a notable increase in the surface area, porosity, and adsorption efficiency of these materials. Their application in the removal of heavy metals, dyes, and other pollutants have shown significant promise, with removal efficiency exceeding 85% in many cases. Nevertheless, the conversion of coconut husk into advanced carbon-based adsorbents using innovative methods such as Hummer's method, remains underexplored. Furthermore, the targeted application of these materials for the removal of methylene blue from wastewater is understudied, particularly with regard to adsorption kinetics and isotherm modelling. In order to address these critical gaps, this research project focuses on synthesising and characterising carbon-based adsorbents derived from coconut husk through Hummer's method. This study aims to comprehensively evaluate the adsorption capacity and kinetics in removing methylene blue of these materials, helping to create sustainable, innovative and effective solutions for wastewater treatment.

CHAPTER 3

METHODOLOGY

3.1 Materials

The coconut husks were sourced from the local market in Kuching, Sarawak. The chemicals used were of analytical reagent grade and were not further purified. The materials required for the fabrication of carbon-based material, including iron (III) chloride($FeCl_3 \cdot 6H_2O$), sodium nitrate($NaNO_3$), sulfuric acid(H_2SO_4), potassium permanganate($KMnO_4$), hydrogen peroxide(H_2O_2), and methylene blue were purchased from Sigma-Aldrich Co. LLC. A stock solution of 100 ppm was prepared by dissolving 0.1g of the methylene blue powder in 1000 mL of distilled water. The working solutions were prepared by diluting the stock solutions to the desired concentrations. The initial pH value was adjusted to the desired level using hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions, according to the experimental design. The pH measurement was conducted using the Thermo Scientific™ Orion Star™ portable pH meter equipped with a combined electrode. All chemicals were used as obtained.

3.2 Synthesis of graphite powder

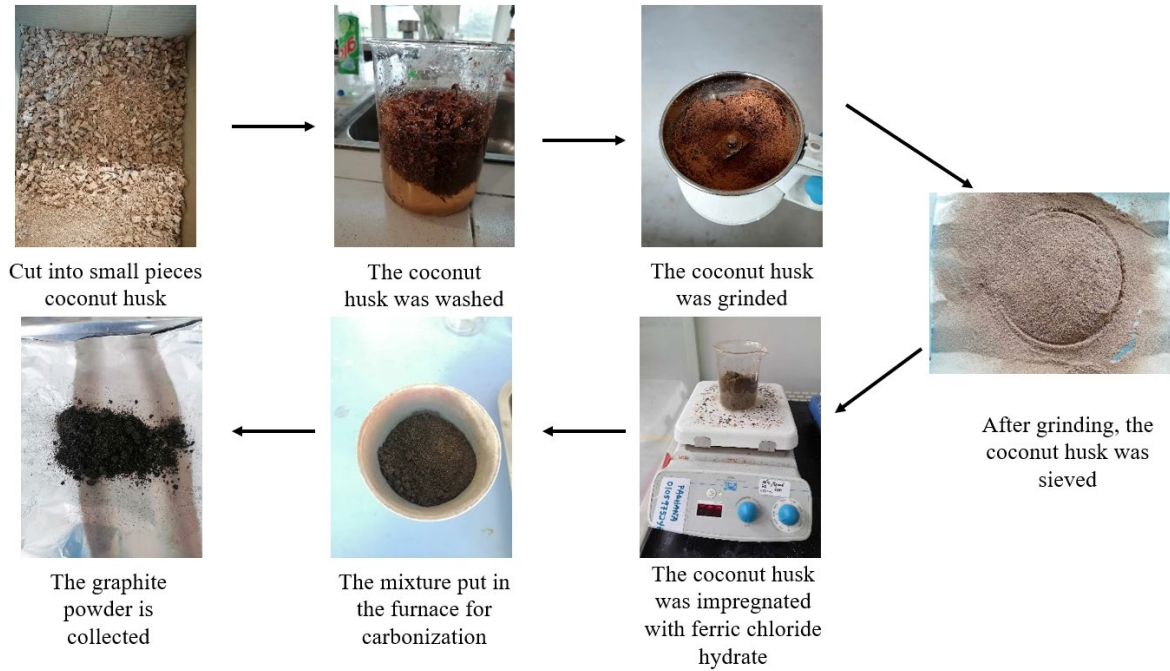


Figure 3.1: Schematic representation of getting graphite powder from coconut husk

The synthesis method (catalytic graphitization) of graphite powder from coconut husk was adopted from (Sujiono et al., 2020). Figure 3.1 shows the steps of synthesis of graphite powder and coconut husk as a precursor. The original coconut husks were sourced from a local market in Kuching, Sarawak. The fibers were extracted, thoroughly washed, and separated from the husks being dried in an oven at 110°C for one day. Throughout the process, precise technical terminology was used to provide clarity and objectivity. The resultant sample was impregnated with $FeCl_3 \cdot H_2O$ at a 1:1 ratio by mixing both components with 10 mL distilled water. The combination mixture was stirred at 200 rpm for 2 hours, ensuring thorough mixing, followed by oven drying at 120°C for 15 minutes. The treated sample was subjected to carbonization in a furnace at 600°C, employing a heating rate of $20^\circ C \text{ min}^{-1}$. To prevent any oxidation, the crucible was enveloped in aluminum foil. This carbonization process kept at a constant temperature for 3 hours, yielded high-carbon

coconut husk charcoal (Nicholas et al., 2018), which was subsequently ground into granular particles with a size ranging from 1 – 2 mm and named coconut husk original. Following this, the ground sample was sieved through a mesh sieve of under two hundred, to ensure a consistent particle size of 1 – 2 mm. Afterwards, the sample was subjected to washing with a 40% concentration of hydrochloric acid (HCl) to remove the impurities compounds such as silica and calcium carbonate are the predominant components found in the biomass (Rukman et al., 2019; Zhang et al., 2018). The sample was subjected to an acid treatment at a ratio of 1: 3 (mass, g to volume, mL) and maintained at 45°C for 3 hours. Following this, washing with distilled water and sodium hydroxide (NaOH) continued until reaching a pH of 7. The final step involved drying the sample in an oven at 110°C for 24 hours to eliminate the residual water and vapour.

3.2.1 Synthesis of coconut husk-derived carbon-based material powder

The synthesis method of graphite powder from coconut husk was adopted from (Sujiono et al., 2020). The modified Hummers method was utilized to synthesis carbon-based material. One gram of the graphite-based powder synthesized from coconut husk and 0.5 gram of sodium nitrate, NaNO_3 were mixed into 25 mL of sulfuric acid, H_2SO_4 . The mixture was stirred for 30 minutes in an ice bath. After the stirring process, 3 grams of the potassium permanganate, KMnO_4 was slowly added to the solution, and the stirring was continued for 3 hours at 20 °C in an ice bath until the solution acquired a dark green colour. The solution was stirred and kept at a constant temperature of 35°C for an additional one hour after being taken out of the ice bath. Gradually, 50 mL of distilled water was added to the mixture and stirred for another 1 hour. Following that, another 100 mL of distilled water was directly added, and the mixture was sterilized for 1 hour. To remove excess potassium permanganate KMnO_4 , 5 mL of hydrogen peroxide was added and stirred for 30 minutes.

Then, the mixture was separated into precipitate and liquid using centrifugation and filtration. The distilled water was added until pH 7 was reached. Finally, the resulting precipitate was then subjected to a temperature of 110°C for 24 hours in an oven, resulting in the creation of carbon-based material powder. The detail steps of the coconut husk-derived carbon-based material is shown in below (Figure 3.2).

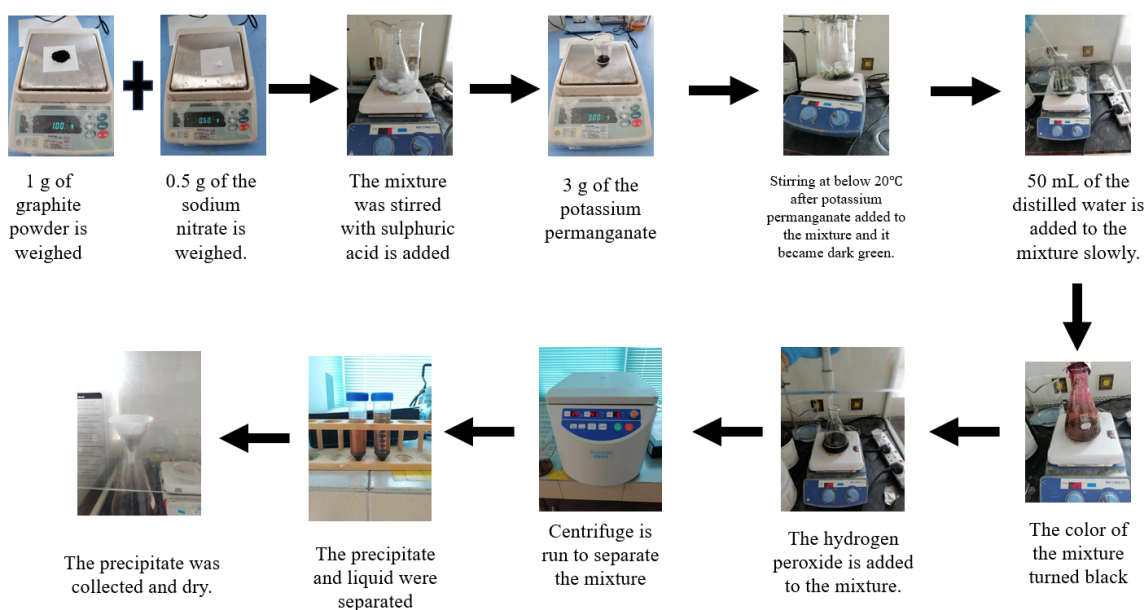


Figure 3.2: Schematic diagram of synthesis carbon-based material

3.3 Adsorbate preparation

A stock solution of methylene blue (MB) dye at a concentration of 1000 mg/L was prepared by dissolving precisely measured 1 g of analytically graded methylene blue in 1000 cm³ of double distilled water. To adjust the pH of the adsorbent – water suspension, the pH of the stock dye solution was maintained at the same level. Different concentrations required for the experiment were attained by diluting the stock solution of methylene blue dye solution, and various initial concentrations for the batch equilibrium studies were prepared via a sequential dilution method.

3.4 Batch adsorption studies

Batch adsorption experiments were conducted to investigate the impact of each selected parameter, within a predetermined range, on the functionality of carbon-based material synthesized from coconut husk. In each study, 100 mL of a methylene blue solution with a known concentration was added to a 250 mL Erlenmeyer flask. The study investigated various experimental parameters, including pH levels (ranging from 3 to 10), the dosage of the adsorbent (varying from 0.02 to 0.01 g), temperature (ranging from 298 to 358 K) and initial adsorbate (methylene blue) concentration (ranging from 5 to 25 mg/L). To estimation the residual concentration of methylene blue (MB) in the solution, samples were collected at predetermined time intervals were centrifuged (4100 rpm; 20°C; 8 minutes) and analyzed using UV – vis spectrophotometer ($\lambda_{\text{max}} = 664 \text{ nm}$). All experiments were conducted three times to reduce the experimental error and the results were presented as the mean value.

3.4.1 Adsorption isotherm experiment

The adsorption equilibrium study was investigated by agitating a series of vials containing 0.1 g of carbon-based material and 100 mL of methylene blue solutions with varied initial concentrations (5 – 25 mg/L). The agitation occurred on a magnetic stirrer hot plate at a constant speed of 200 rpm and a temperature of $25 \pm 2^\circ\text{C}$. The agitation was continued at the desired temperature for 1 hour, and the samples of methylene blue solution samples were analysed to determine the concentration.

3.4.2 Effect of pH study

The method of adsorption of effect of pH study experiment was adopted from (Aljeboree et al., 2017). The impact of pH on the methylene blue adsorption to carbon-based material was studied by altering the pH at 3, 5, 7, 8, and 10 using solutions of methylene

blue at a fixed concentration of 15 mg/L. Meanwhile, the weights of the adsorbents used were 0.1 g for the five different pH analysed. The pH value was regulated using weak sodium hydroxide, NaOH and weak hydrochloric acid, HCl. The adsorbents were put into methylene blue solutions for 24 hours at room temperature. The centrifugation method was utilized for separation, and a UV-Vis spectrophotometer was employed to measure the obtained filtrate.

3.4.3 Adsorbent dosage study

Carbon-based material was used in varying dosages between 0.02 – 0.1 g in increments of 0.02 g, whilst being exposed to a methylene blue solution with concentrations of 15 mg/L in 100 mL. The adsorbents were left to stir with the methylene blue solution for 24 hours at room temperature. Then, the adsorbent was separated from each dye solution using centrifugation. The separated solution was measured for absorbance value using a UV – Vis spectrophotometer.

3.4.4 Initial adsorbate concentration study

The impact of methylene blue concentration on the adsorption process of methylene blue onto the adsorbents was investigated by varying the methylene blue concentrations in the range of 5 – 25 mg/L at 5 mg/L intervals specifically for carbon-based material sample, which weighted 0.1 g. The experiments were carried out at room temperature for a period of 24 hours. Following the experiments, the adsorbents were separated from each dye solution using centrifugation. Subsequently, the absorbance value of the separated solution was measured using a UV – Vis spectrophotometer.

3.4.5 Effect of temperature study

The study focused on the adsorption of dyes on carbon-based material particles. A constant concentration of 15 mg/L was applied while using 0.1 g of carbon-based material

particles at variable temperatures of 25, 35, 55, 65, and 85°C. Technical abbreviations were first explained. The experiment lasted for 1 hour with stirring at a specific temperature. After the stirring, the adsorbent was separated from each dye solution using centrifugation. The separated solution was measured for absorbance values using a UV – Vis spectrophotometer.

3.4.6 Effect of contact time

The method of adsorption of effect of contact time experiment was adopted from (Ogata et al., 2020). 0.1 g of the carbon-based material was added to the methylene blue solution with a concentration of 15 mg/L as much as 100 mL. The mixture was then stirred with a variation of adsorption contact time of 1,3, 6, 8, 18, 19, 20, 21, 22, 23, 23.15, 23,30, 24, and 24.5 hours to observe the adsorption process. After the stirring, the adsorbent was separated from the dye solution. Furthermore, a UV – Vis spectrophotometer measured each solution for its absorbance value.

3.5 Characterization of carbon-based material

3.5.1 Fourier transform infrared (FTIR)

The Fourier transform infrared spectra were analysed before and after the adsorption of carbon-based material. The spectroscopic analyses facilitate the examination of the surface chemistry of the carbon-based material powder before and after adsorption. The FTIR spectra provide comprehensive information on the functional groups' characteristics on the surface of carbon-based material powders, both before and after adsorption. The carbon-based material is in powder form which suitable for FTIR analysis. The functional groups on the surface of biomass-derived carbon-based material were using the attenuated total reflectance (ATR) technique in conjunction with Four Transform Infrared (FT-IR) Spectroscopy (Shimadzu IRAffinity-1, Japan) before and after dye adsorption. The samples

were pressed against a horizontally positioned diamond prism for infrared microscope analysis, and the recorded infrared spectra covered the IR wavelength range of 4000 to 400 cm^{-1} . The spectra data were acquired with twenty scans at a resolution of 4 cm^{-1} and plotted on the transmittance axis using a consistent scale (Lee et al., 2017).

3.5.2 Scanning electron micrograph (SEM) and Energy – dispersive X-ray (EDX)

The surface morphology of the carbon-based material was examined using a Hitachi TM 4000PLUS, Japan scanning electron microscope (SEM), which was equipped with an embedded energy dispersive X-ray analyser (EDS) for the elemental analysis. For SEM analysis, the dry sample was mounted on aluminium plates using double-sided conductive carbon tape. On the other hand, the specimen surface underwent qualitative EDS spectrum analyses at an accelerating voltage of 15kV, while maintaining an analytical working distance of 10 mm (Lee et al., 2017).

3.6 Data Analysis

3.6.1 Percentage of methylene blue removal by carbon-based material

The equilibrium concentration of dye, q_e ($mg\ g^{-1}$), was calculated from the mass balance Equation (3.1):

$$q_e = \frac{(C_i - C_e)V}{m} \quad \text{Equation 3.1}$$

Where, C_i ($mg\ L^{-1}$) = initial dye concentration, C_e ($mg\ L^{-1}$) = equilibrium dye concentration in solution, V (L) = volume of the test solution, and m (g) = mass of adsorbent (carbon-based material) used.

The percentage of dye removal (%) was determined as Equation (3.2):

$$Removal (\%) = \frac{(C_i - C_e)V}{C_i} \times 100 \quad \text{Equation 3.2}$$

3.6.2 Process isotherm

Different isotherm models were employed to examine the relationship between the equilibrium dye concentration on carbon-based material (q_e) and the equilibrium dye concentration in the solution (C_e). In the present investigation, the results of adsorption studies of dye at various temperatures onto carbon-based materials were fitted to models of Freundlich, Langmuir and Temkin models. The correlation coefficient of each model was also determined (R^2) for comparative analysis of best fit. Investigating different isotherm parameters for Methylene blue adsorption by carbon-based material.

Langmuir model:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad \text{Equation 3.3}$$

Where, C_e = Equilibrium dye concentration in solution (mg L^{-1}), q_e = Equilibrium dye concentration on carbon-based materials (mg g^{-1}), K_L = Langmuir constant (L mg^{-1}), q_m = Maximum adsorption capacity (mg g^{-1}). The Langmuir equation was showed in equation (3.3).

Freundlich model:

$$\log q_e = \frac{1}{n} \ln C_e + \ln K_F \quad \text{Equation 3.4}$$

Where, q_e = Equilibrium dye concentration on carbon-based materials (mg g^{-1}), n = Freundlich adsorption isotherm constant, C_e = Equilibrium dye concentration in solution

(mg L^{-1}), K_F = Freundlich constant (mg g^{-1}) (L g^{-1}) $^{1/n}$. The Freundlich equation was showed in equation (3.4).

Temkin model:

$$q_e = B \ln C_e + B \ln K_T \quad \text{Equation 3.5}$$

B = Coefficients of heat of adsorption calculated from slope of q_e vs $\ln C_e$ plot at operational temperature T (298 K) (J mol^{-1}), K_T = Temkin equilibrium binding constant calculated from intercept of q_e vs $\ln C_e$ plot at operational temperature T (298 K) (L g^{-1}), R^2 = Correlation coefficient. The Temkin equation was showed in equation (3.5).

3.6.3 Process of adsorption kinetics model

The study of adsorption kinetics described the adsorbate uptake rate and evidently, this rate controlled the residence time of adsorbate at the solid-liquid interface. In order to analyse the adsorption kinetics of methylene blue onto carbon-based material, Lagergren's pseudo-first-order and Ho-McKay's pseudo-second-order models were applied to the experimental data. Data obtained from batch studies were fitted to the Lagergren pseudo-first-order (Lagergren, 1898), and pseudo-second-order (Ho and McKay, 1999) models at different temperatures (298 – 318 K). Adsorption capacity denoted dye adsorbed at any time (t) respectively. The activation energy, for methylene blue adsorption by carbon-based material was calculated from the slope of the Arrhenius plot of $\ln k$ vs. $T^{-1/2}$ governed by the equation from (3.6) to (3.7) given below (Anirudhan & Radhakrishnan, 2008).

Whereby, k = kinetic constant, A = pre-exponential factor, R ($8.314 \text{ J mole}^{-1} \text{ K}^{-1}$) = ideal gas constant and T (K) = absolute experimental temperature respectively.

Comparative analysis of the correction coefficient (R^2) determined for each model indicated the one most appropriate for methylene blue adsorption by carbon-based materials.

Analysis of kinetic parameters for methylene blue adsorption by carbon-based materials

Pseudo – first order

$$\log(q_e - q_t) = \left[\log q_e - \frac{k_1}{2.303} t \right] \quad \text{Equation 3.6}$$

Where, k_1 = Pseudo-1st order rate min^{-1} constant plots of $(q_e - q_t)$ vs t (min^{-1}), q_e (mg g^{-1}) = quantity of dye adsorbed at equilibrium, R^2 = correlation coefficient

Pseudo – second order

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Equation 3.7}$$

Where, k_2 = Pseudo-2nd order rate constant determined from plot of $1/q_t$ vs t ($\text{mg g}^{-1} \text{min}^{-1}$), q_e = Quantity of dye adsorbed at equilibrium (mg g^{-1}), R^2 = correlation coefficient

3.6.4 Process thermodynamics

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Therefore, Gibbs free energy change ($\Delta G^\circ \text{ kJ mol}^{-1}$), enthalpy ($\Delta H^\circ \text{ kJ mol}^{-1}$) and entropy ($\Delta S^\circ \text{ J mol}^{-1} \text{K}^{-1}$) were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. Thermodynamic parameters were calculated by applying the equations from (3.8) to (3.10):

$$\Delta G^\circ = -RT \ln K_c \quad \text{Equation 3.8}$$

$$K_c = \frac{C_a}{C_e} \quad \text{Equation 3.9}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{Equation 3.10}$$

Where, C_a = equilibrium dye concentration on the carbon-based material ($mg L^{-1}$), C_e = equilibrium dye concentration in solution ($mg L^{-1}$), R = universal gas constant ($8.314 J mol^{-1} K^{-1}$), T = absolute operational temperature (K), K_c = distribution coefficient for adsorption. ΔH° and ΔS° were determined from the slope and intercept of a linear plot of ΔG° VS. T respectively.

3.7 Statistical analysis

The experimental results were obtained three times and expressed as a mean using Microsoft Excel. The purpose of the statistical analysis is to evaluate the significance of adsorption parameters. The experimental data is fitted to various isotherm and kinetic models to determine the correlation coefficients (R^2) and evaluate the goodness of fit.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Calibration curve

A stock solution of 1000 mg L^{-1} methylene blue dye was prepared. Various concentration ($10 - 400 \text{ mg L}^{-1}$) of the methylene blue dye were prepared from stock solution and were read on a UV – vis spectrophotometer. A calibration curve of absorbance against methylene blue dye concentrations (in the range of $(10 - 400 \text{ mg L}^{-1})$ at pH values between 7.04 and 7.5. The experimental data reported in Figure 4.1 were fitted by a straight line with a high correlation coefficient ($r^2 = 0.9931$). The high correlation coefficient found in the calibration curve in the current study suggests that the molar absorptivity continues constant throughout the concentration range studied. Therefore, allows for the accurate determination of the concentration of methylene blue dye concentration (Unuabonah et al., 2009).

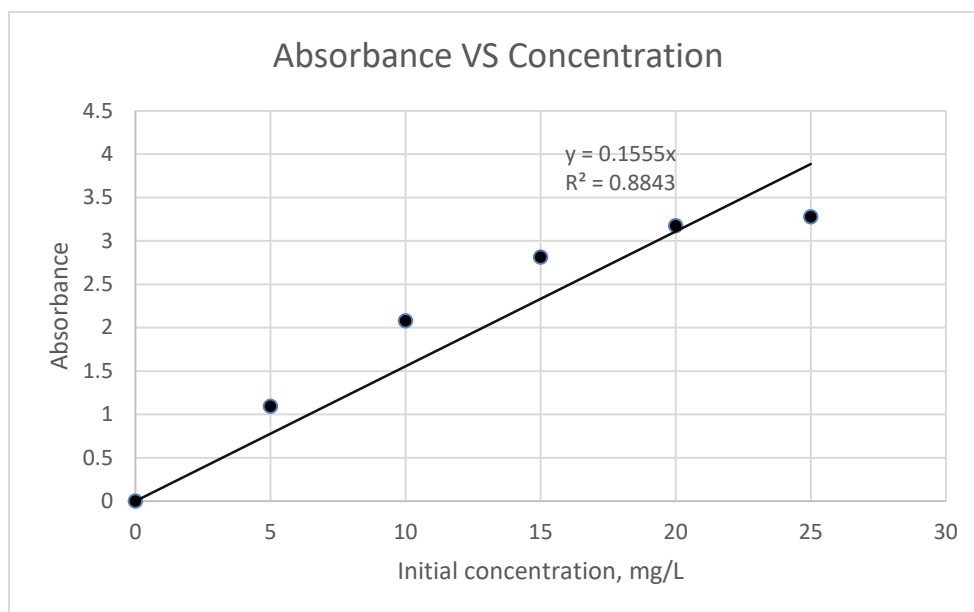


Figure 4.1: Calibration curve for determination of adsorbance

4.2 Adsorbent characterization

4.2.1 Scanning electron microscopy – energy dispersive X – ray analysis (SEM-EDX)

In Figure 4.2 (A) and (B), the SEM images offer a comprehensive visualisation of the surface morphology of the carbon-based material, clearly demonstrating the presence of pores of varying dimensions. This porous structure is attributed to the volatilisation of substances during the thermal decomposition of lignocellulosic components, whereby the escape of these volatiles at elevated temperatures facilitates the formation of irregularly shaped pores. As the temperature increases, the materials' microstructure undergoes degradation, resulting in a rougher surface characterised by particulate and blocky fragments. This phenomenon is attributed to the gradual breakdown of biomass under extreme thermal conditions, leading to significant ash accumulation on the surface (Luo et al., 2024). Conventional graphitization without iron preserves the macrostructure of biomass; however, the introduction of iron catalysts markedly enhances microporosity through the formation of graphitic nanostructures (Hunter et al., 2022). Figure 4.2 (C) depicts

the materials' surface post-adsorption, illustrating a noticeable reduction in pore visibility and an increasingly coarse texture compared to Figure 4.2 (A) and (B). This transformation is attributed to the deposition of methylene blue dye, which coats the surface, obscuring the pores (Sawasdee & Watcharabundit, 2023). Mosoarca et al. (2020) further corroborated these findings, noting that prior to adsorption, the adsorbent surface is characterised by an abundance of pores of varying shapes and sizes, providing numerous active sites for dye adsorption. Subsequent to the adsorption process, methylene blue molecules become embedded within these pores, resulting in a state of complete saturation and coverage of the surface with dye molecules. In order to provide a comprehensive assessment of the elemental composition and purity of the carbon-based material, an integrated approach was employed, utilising both SEM analysis and EDX data. This comprehensive approach enabled the identification of key constituents, including carbon (C), oxygen (O), chlorine (Cl), and iron (Fe). The EDX analysis yielded mass percentages of 71.55% carbon (C), 18.55% oxygen (O), 2.31% chlorine (Cl), and 7.59% iron (Fe), providing a quantitative basis for material's elemental composition. The atomic composition of the material was also analysed, with carbon and oxygen found to be the primary elements, accounting for 81.41% and 15.85% of the atoms, respectively. The presence of chlorine and iron was found to be unexpected, and was attributed to incomplete washing during synthesis, with residual chlorine from hydrochloric acid and iron from iron (III) chloride hydrate, used as a catalyst, being retained due to time constraints in the washing process (see Table 4.1 for details). There was similar a study by Thabede (2023) found that the activated carbon mandarin orange peels still observed chloride (Cl) traces after washing process. Subsequent EDX analysis of the methylene blue-loaded material revealed the presence of additional elements, including nitrogen, sulfur, and chlorine, thereby confirming the efficacy of the adsorption process.

Notably, the presence of sulfur can be attributed to the methylene blue dye, indicative a well-distributed array of active adsorption sites. These findings align with those that have been stated by Elkholy et al. (2023), who discovered nitrogen, sulfur, and chlorine in the EDX spectra of similar samples, thus confirming the effective adsorption of methylene blue. Finally, analysis of BET surface area indicated a specific surface area of $68.443\text{ m}^2\text{g}^{-1}$ for the carbon-based material, highlighting its substantial potential for adsorption applications.

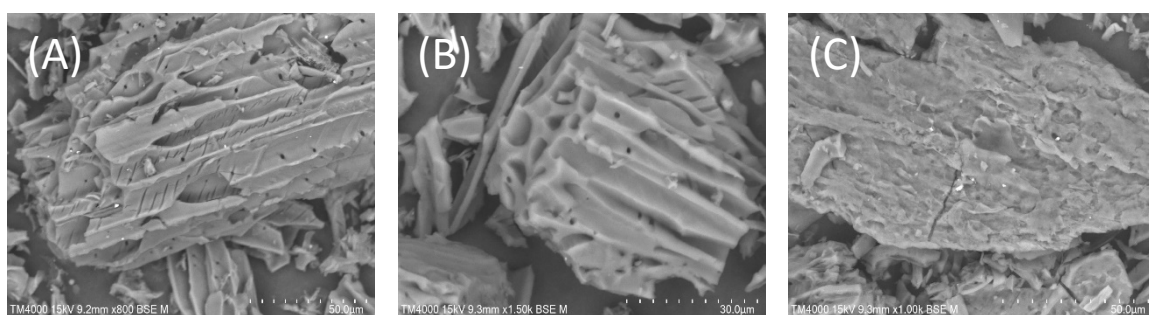


Figure 4.2: (A), (B) are SEM images of carbon-based material before adsorption and (C) is SEM image of carbon-based material after adsorption

Table 4.1: EDX data of carbon-based material before and after adsorption

Element	Carbon-based material before adsorption		Carbon-based material after adsorption	
	Mass, %	Atom, %	Mass, %	Atom, %
Carbon, C	71.55	81.41	62.51	70.32
Oxygen, O	18.55	15.85	30.15	25.47
Chlorine, Cl	2.31	0.89	0.82	0.31
Iron, Fe	7.59	1.86	2.78	0.67
Nitrogen, N	0	0	3.04	2.93

Table 4.1 continued

Sulfur, S	0	0	0.70	0.30
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4.2.2 Fourier Transform Infrared (FTIR) analysis

Fourier Transform Infrared (FTIR) spectroscopy is a powerful analytical tool that can be used to identify surface functional groups and elucidate their critical role in the mechanisms of dye adsorption. These functional groups significantly influence the interaction between adsorbate molecules and the surface of the adsorbent, thereby governing the overall efficiency of adsorption. The FTIR spectra of the carbon-based material, both prior to and following methylene blue adsorption, are presented in Figure 4.3 and Figure 4.4, providing valuable insights into the chemical modifications occurring during the adsorption process. According to the Figure 4.3, the peaks in the range of approximately 2000 cm^{-1} to 2363.82 cm^{-1} is associated with the $\text{O}=\text{C}=\text{O}$ stretching vibration (Jahan et al., 2022). The peaks at 1533 cm^{-1} corresponds to NH_3^+ (Sultana et al., 2022), while the peak at 1740 cm^{-1} represents the $\text{C}=\text{O}$ stretching frequency of the $-\text{COOH}$ group (Verma & Dutta, 2015). The stretching modes of $\text{C}=\text{O}$ bonds are generally considered as the signature of carbon-based material, the evidence that graphite had been oxidized (Olorunkosebi et al., 2021). The carbon-based material synthesized from the coconut husk exhibits a limited presence of functional groups. The amount of oxygen functional groups in the carbon-based material was observed to be low due to partial oxidation, as illustrated in Figure 4.3. An analogous investigation by Krishnamoorthy et al. (2013) also noted low levels of oxygen functional groups in similar study. From Figures 4.3 and 4.4 which show before and after methylene blue adsorption on the carbon-based material, there were distinct variations in the spectra.

The spectrum shows that upon adsorption of methylene blue, the change of the intensity of infrared bands took place without any change of the positions. The changes in the FTIR spectra along with the results assure that the process includes incorporation of methylene blue along with the functional groups contained in the carbon-based material.

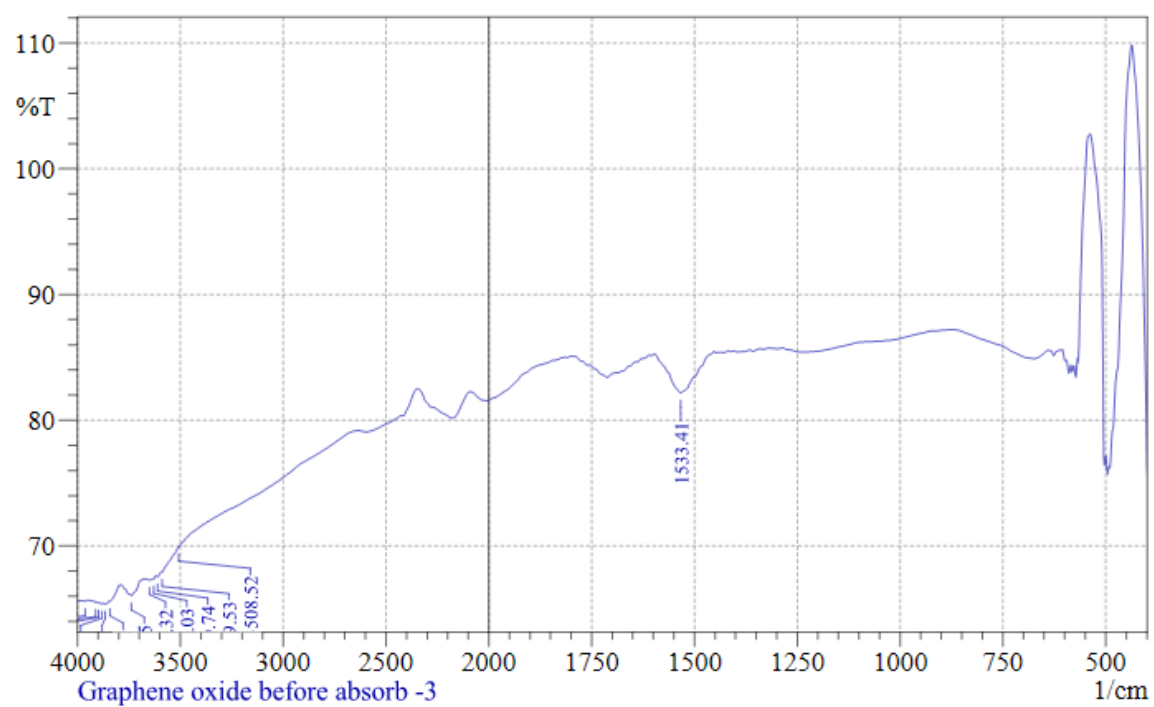


Figure 4.3: FTIR spectra of carbon-based material before adsorption

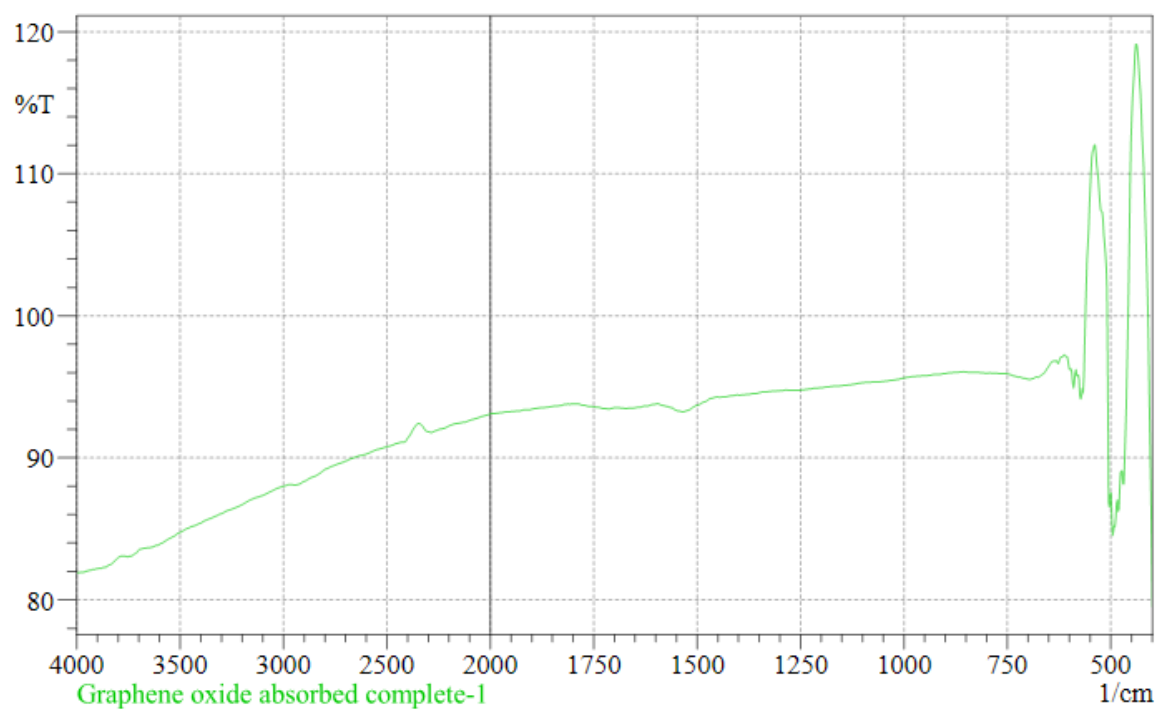


Figure 4.4: FTIR spectra of carbon-based material after adsorption

4.3 pH study on carbon-based material adsorption

The pH water is carefully monitored due to its crucial role in determining the level of adsorption as it affects both the surface charge of the adsorbent as well as the ionization state of the adsorbate particles (Ahmad et al., 2020; Tang et al., 2017). An abundance of H^+ ions result in an increase in the positive charge on the adsorbent surface under acidic pH conditions. This subsequently results in the electrostatic repulsion of cationic methylene blue molecules and the adsorbent, which also harbors a positive charge, resulting in reduction of the total adsorption effectiveness (Chahm et al., 2018). Moreover, the competitive interaction between H^+ ions and methylene blue cations for the available adsorption sites further contributes to the decline in adsorption capacity under lower pH conditions. Conversely, when the pH of the solution risen results in the adsorbent surface undergoing deprotonation, acquiring a net negative charged. This, in turn, enhances electrostatic attraction between the negatively charged adsorbent and the positively charged methylene blue molecules, thereby facilitating greater adsorption. The pH of the solution plays a pivotal role in regulating not only the surface characteristics of the adsorbent but also the fundamental interactions governing the adsorption mechanism (Lelifajri et al., 2020). To this end, experimental investigations were conducted at were 298 K to investigate how pH affects the adsorption of methylene blue adsorption. The pH was systematically adjusted to 3, 5, 7, 8 and 10 using 0.1 M hydrochloric acid or 0.1 M sodium hydroxide. Subsequently, 0.1 g of the carbon-based material added to each solution. Following a 24– hours equilibration period, measurements were recorded for both dye concentration and adsorption efficiency. Figure 4.5 clarifies the way pH influences methylene blue adsorption at a starting concentration of 15 ppm and indicates that pH and adsorption capacity are positively correlated. The outcomes demonstrate that the capacity of carbon-based materials to adsorb methylene blue

is significantly impacted by high pH levels. As illustrated in Figure 4.6, 15 mg/L was the initial concentration of methylene blue, the adsorption capacity at a pH of 3 was determined to be 5.4 mg/g. However, this capacity underwent a substantial increase to 10.15 mg/g at a pH of 10.00, underscoring the considerable influence of pH on the efficacy of adsorption. Two fundamental mechanisms have been identified as the driving forces behind this trend. Firstly, when the pH values were lower, the presence of H^+ ions saturate the active sites of the adsorbent, thereby reducing the quantity of binding sites that are available for methylene blue adsorption. Secondly, adsorption efficiency is further limited by the effect of protonation of the adsorbent surface at low pH, which increases positive charge and increases electrostatic repulsion with the cationic dye molecules. Consequently, enhanced methylene blue uptake. When pH levels become higher, the surface of adsorbent becomes predominantly negatively charged, thereby facilitating stronger electrostatic interactions with methylene blue cations and ultimately enhancing adsorption efficiency (Suma et al., 2021). The pH range of 7 to 10 has been identified as the optimal adsorption performance of carbon-based material, with a maximum adsorption capacity of 10.15 mg/g. This trend aligns with the findings of previous studies, such as those conducted by Yao and Zhang, which similarly reported enhanced methylene blue adsorption under alkaline condition (Yao et al., 2020; Zhang et al., 2020). Moreover, analogous results have been documented for various dye adsorption studies, thereby confirming that the adsorbent exhibits a net positive charge under acidic conditions, which in turn diminishes adsorption efficiency (Demirbas, 2009; Kavitha & Namasivayam, 2007).

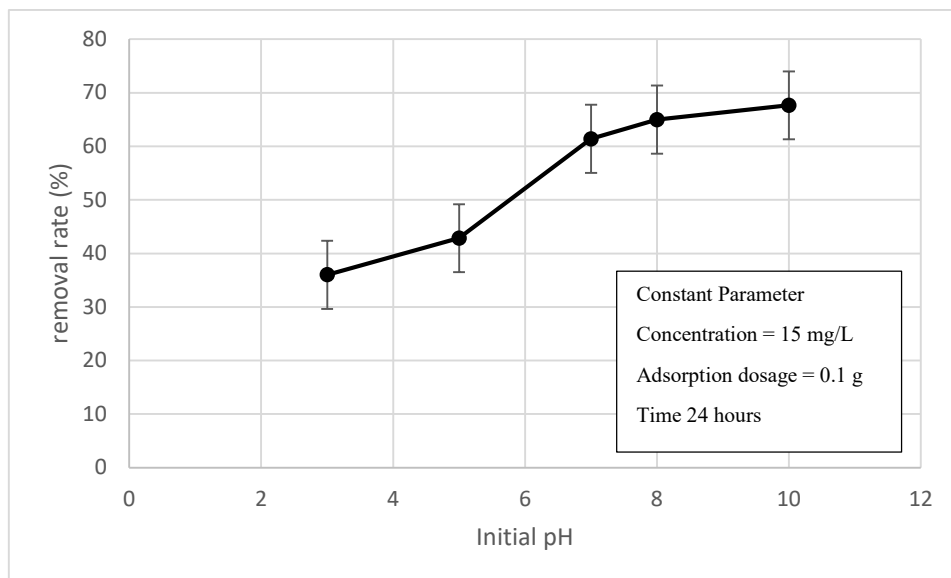


Figure 4.5: The removal rate of methylene blue on the carbon-based material

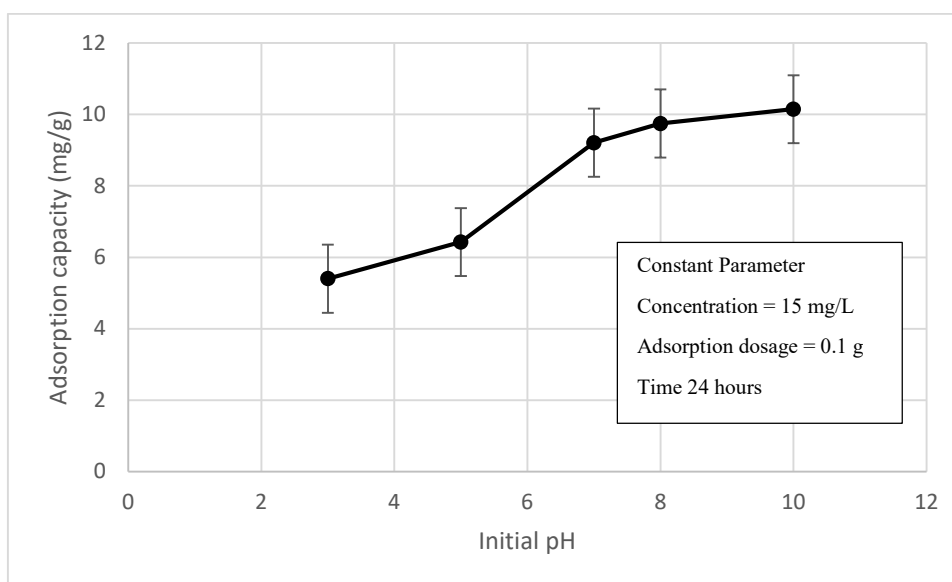


Figure 4.6: The adsorption capacity of methylene blue on carbon-based material

4.4 Adsorbent dosage study

Adsorbent dosage is pivotal in determining the overall efficiency of the adsorption process, directly influencing the availability of active binding sites and the extent of dye removal (Salleh et al., 2011). This study systematically evaluated the effect of varying adsorbent dosages on methylene blue adsorption, establishing the optimal amount required

for different dye concentrations. Specifically, experiments were conducted using a fixed methylene blue concentration of 15mg/L in 100 mL of solution, while adsorbent dosages were incrementally varied across five levels (0.02g, 0.04g, 0.06g, 0.08g, and 0.1g), as illustrated in Figure 4.7. The findings revealed a direct correlation between increasing adsorbent dosage and enhanced adsorption efficiency, following the expected trend observed in previous studies (El-Katori et al., 2011). The described phenomenon can be attributed to greater availability of adsorption sites which increases as the methylene blue adsorbent dosage increases. The 0.02g increments may interrelate because the mass transfer resistance of the dye molecules in solvent and adsorbing surface decreases with adsorbent increasing. The more the adsorbent is added, the more the system becomes rich in pores and active sites, making the system more permeable to dyes (Ho et al., 2005). Consequently, at a constant initial dye concentration, higher adsorbent dosages provide an augmented surface area, which enhances the adsorption process. When the quantity of the adsorbent increases, a number of active regions grows into accessible, further driving adsorption efficiency (Khattari & Singh, 2009). However, beyond a certain threshold (0.12g), excessive adsorbent loading results in a diminishing rate of adsorption per unit mass. This phenomenon has been previously observed in other studies, including that of Othman et al. (2018) using magnetic carbon-based material. The findings emphasize the importance of optimizing adsorbent dosage to achieve a balance between efficiency and cost-effectiveness in practical applications. Excessive loading of the adsorbent may not only diminish per-unit adsorption capacity but also result in material wastage. The optimal dosage was 0.1g. It is therefore vital to determine an optimal adsorbent dosage, so as to maximize adsorption efficiency while ensuring sustainable and economically viable wastewater treatment solutions.

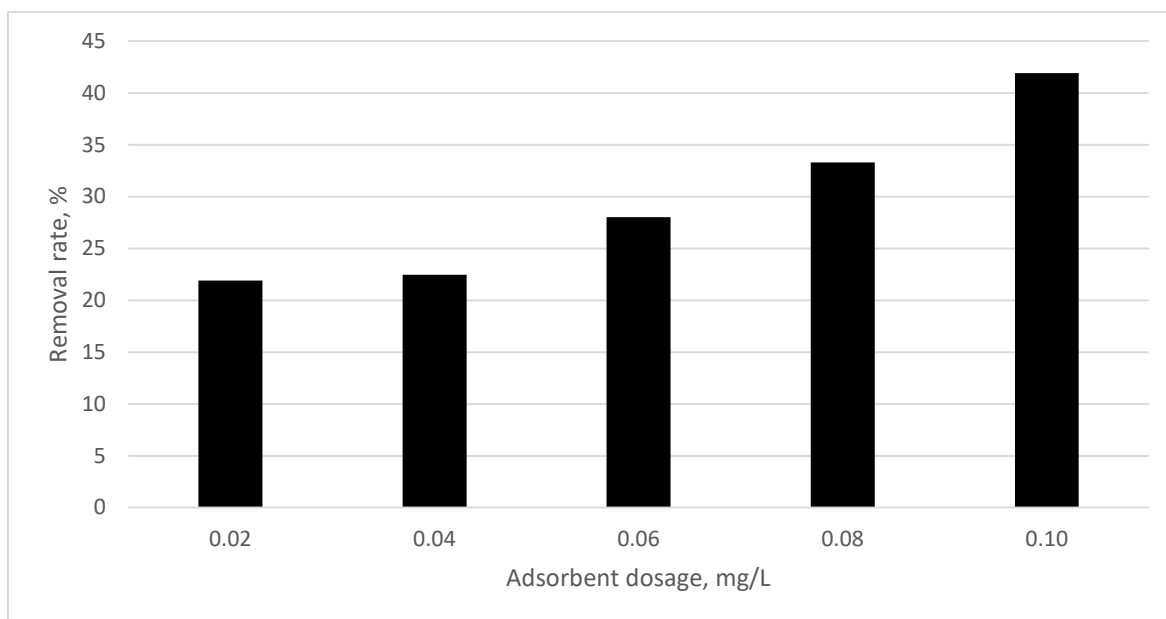


Figure 4.7: Effect of adsorbent dosage on methylene blue on carbon-based material (Equilibrium time =24 hours)

4.5 Contact time study

As shown in Figure 4.8 and 4.9, it is evident that the effect of the contact time on removal rate of and adsorption capacity of methylene blue is a critical factor. It is acknowledged that the contact time is an importance consideration when it comes to performing adsorption, as it signifies the quantity of adsorbate that is accumulated on a specified mass of adsorbent over a given period (Suleman et al., 2021). In this research, the adsorption of methylene blue onto the carbon-based material showed that there was a rapid uptake in the initial phase of contact, the followed by a gradual deceleration until reaching equilibrium. This behaviour indicates that the adsorption rate is predominantly dictated by the large number of active sites on the surface of the adsorbent at the onset. Nevertheless, after some time, those sites become saturated and, therefore, the rate of dye uptake is reduced. The experimental findings also verify that both the adsorption capacity and removal efficiency are enhanced as the contact time is extended, mostly because of the increased

interactions with the adsorbent surface and the contact time because of the higher contact between the surface of adsorbent and dyes molecules (Oetjik & Aida Ibrahim, 2021).

The process exhibited a single – phase and was characterized by a slow adsorption process. After 24–hours duration of the experiment, there was no significant increase in the removal of methylene blue. However, the adsorption rate increased over time and eventually stabilized. This phenomenon can be attributed to the saturation of active adsorption sites on the carbon-based material surface, resulting from the binding relations among molecules and methylene blue and these sites. The initial removal rate is considerably elevated due to the ample accessibility of adsorption sites on the adsorbent's surface. The existence of numerous appropriate bonding sites and expanded surface areas. The adsorption process advances gradually over several hours, until reaching equilibrium. The initial high dye removal is attributed to the abundance of available free binding sites on the adsorbent surface, while the following decline in biosorption rate results from the gradual occupation of these free binding sites (Gemici et al., 2021). Nonetheless, as the adsorption process advances, it reaches a phase where the rate of dye uptake is mainly controlled by the diffusion of dye molecules from the outer surface to the internal adsorption sites within the adsorbent particles. This shift in the rate determining step influences the overall adsorption kinetics (Amin, 2008). Moreover, for the other experiments, the initial concentration of methylene blue was predetermined. Based on previous findings, the initial concentrations chosen for the following experiments were 20, 30, 40 and 50 mg/L. Vassileva et al. (2023) pointed out that with increasing contact time the removal rate of the methylene blue also increased until reaching a maximum.

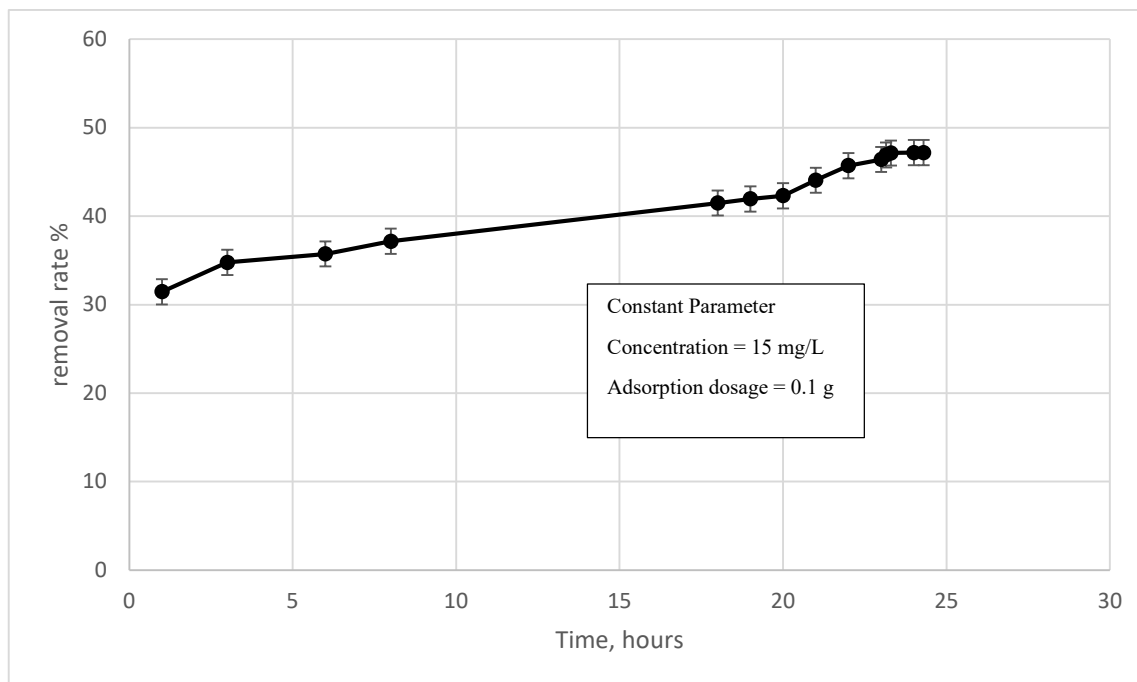


Figure 4.8: The impact of contact duration on the rate of methylene blue on carbon-based material

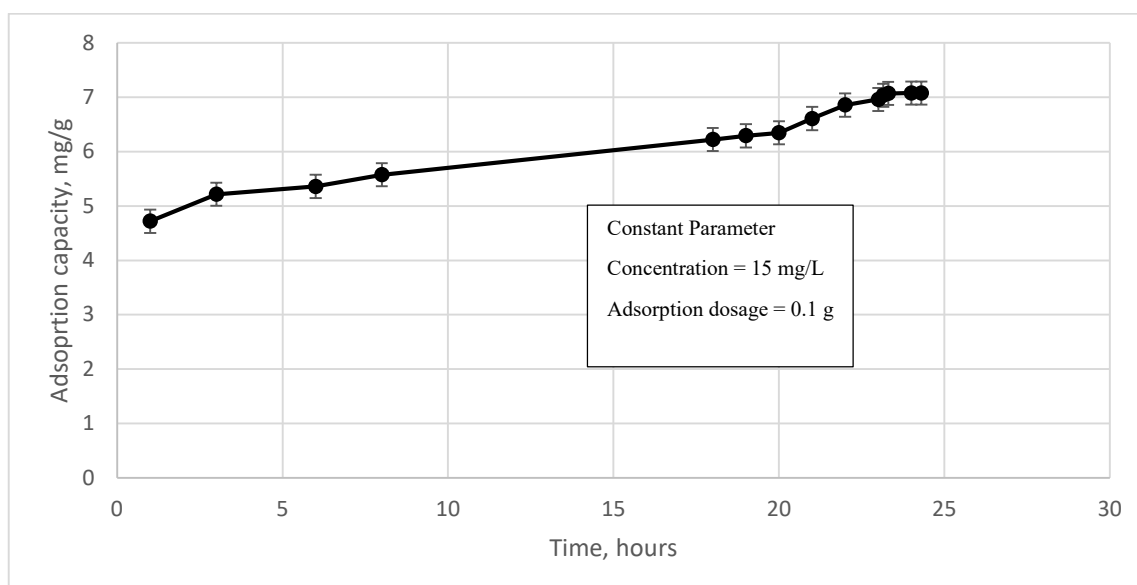


Figure 4.9: The effect of contact time on methylene blue adsorption on carbon-based material and its adsorption capacity

4.6 Dye concentration study

In Figures 4.10 and 4.11, methylene blue is found to be the highest removed rate at low initial concentrations which are 5 mg/L and 10 mg/L, but the adsorption capacity is

lower than the adsorption capacity of 15 mg/L. This trend can be explained by the presence of active adsorption sites on the carbon-based adsorbent, which, at lower dye concentrations, surpasses the amount of dye molecules in solution to an extreme degree. This results in the effective capture of nearly all methylene blue molecules, ensuring complete removal. However, the number of dye molecules exceeds the number of available active sites as the initial dye concentration rises, leading to incomplete adsorption and a subsequent decline in removal efficiency. Despite the decrease in percentage removal, the adsorption capacity initially increases with rising dye concentrations, reaching a peak of 10.88 mg/g at 15 mg/L, before experiencing a slight decline at higher concentrations (9.69 mg/g at 20 mg/L and 9.63mg/g at 25mg/L). At lower concentrations, a steep concentration gradient between the solution and the adsorbent surface facilitates enhanced mass transfer, promoting a higher dye uptake per unit mass. However, beyond an optimal concentration (e.g., 15 mg/L), the saturation of adsorption sites restricts further uptake, resulting in a plateau or minor decrease in adsorption capacity. There was a similar observation by Dawood et al. (2016). However, with higher initial concentrations, the restricted adsorption sites lead to a cap on dye percent removal. The reduction in percentage of dye removal at higher concentrations is due to the increased available adsorption sites, enabling much stronger driving forces for dye diffusion to surface of the adsorbent (Mondal & Kar, 2018; Tejada-Tovar et al., 2021). However, the direct interaction between the dye molecules and the adsorption sites decreases with increasing dye concentration, causing a decline in removal efficiency. The influence of the initial dye concentration on adsorption behaviour is inherently linked to the equilibrium between the dye concentration and the available binding sites on the surface of the adsorbent. In general, the percentage removal of dye exhibits a decline with an increase in dye concentration, given the inherent fixed adsorption capacity of a given mass of adsorbent.

Higher dye concentrations result in a reduction in the volume of solution that can be effectively treated (Bharathi & Ramesh, 2013). For instance, in the context of methylene blue adsorption onto carbon-based materials, a concentration range of 5 – 25 mg/L was observed to demonstrate a negative linear correlation. This implies that an increase in the initial concentration of the dye will decrease the adsorption capability of the adsorbent, which most likely is due to what appears to resistance mechanisms controlling the removal of methylene blue (Rodríguez-Arellano et al., 2021).

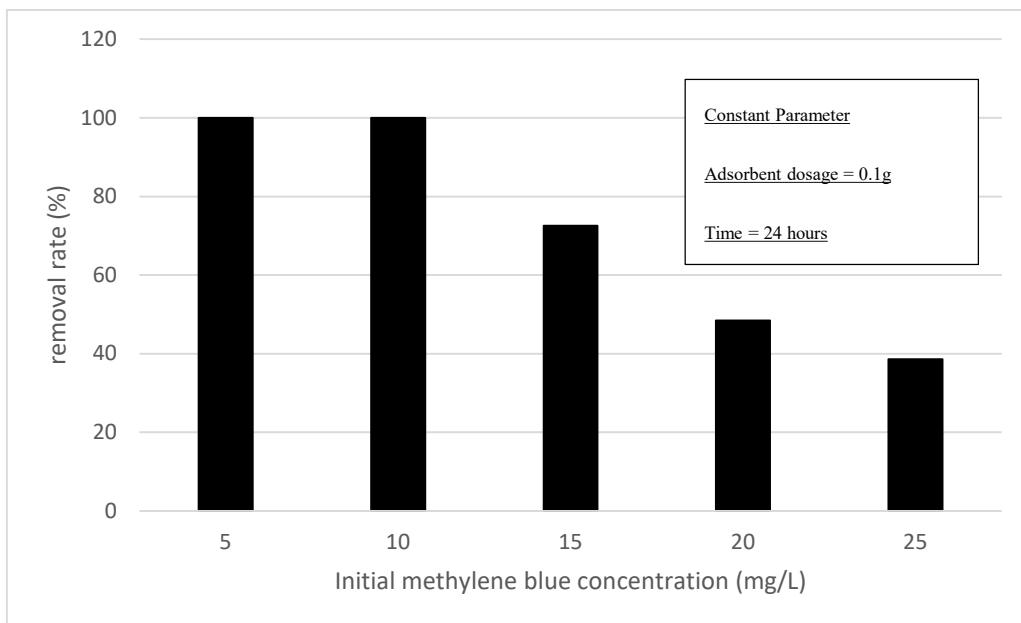


Figure 4.10: Impact of initial concentration of methylene blue on removal rate

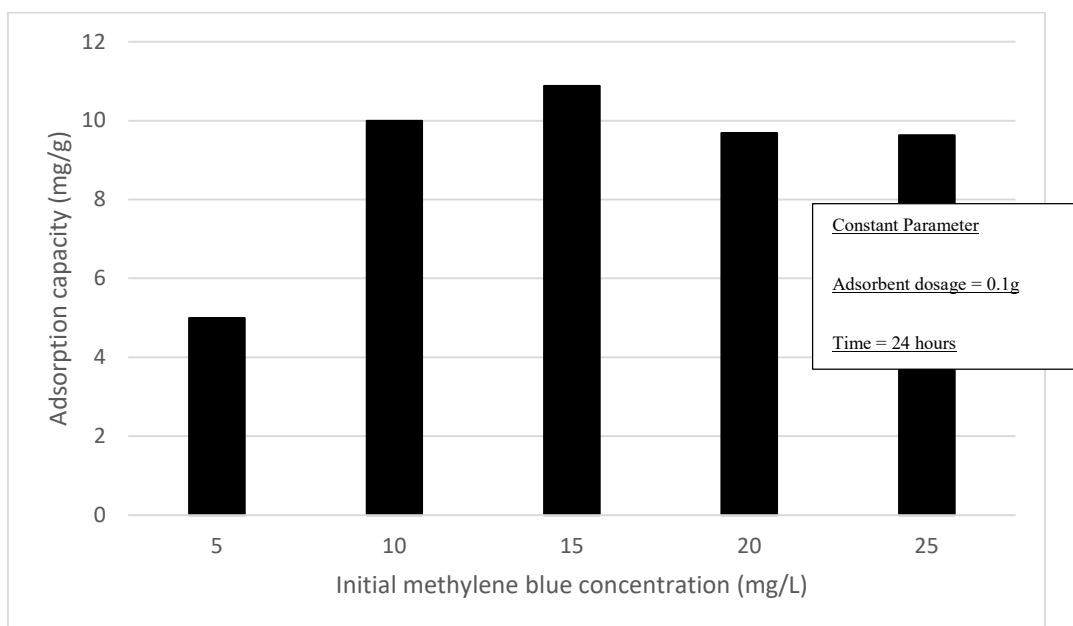


Figure 4.11: Impact of initial concentration of methylene blue on adsorption capacity

4.7 Adsorption Kinetics study

Both the pseudo-first order and pseudo-second-order models were applied to assess the non-linear kinetic modelling of methylene blue adsorption onto the carbon-based adsorbent. The non-linear plots for these models are illustrated in Figure 4.12 and Figure

4.13. The key kinetic parameters - k_1 , k_2 , q_e and n , along with statistical parameters, are comprehensively detailed in Table 4.3. The findings unequivocally demonstrate that the pseudo-second order kinetic model manifests augmented predictive prowess, as substantiated by its elevated coefficient of determination R^2 and diminished sum of squared residuals (SSR) in comparison to the pseudo-first order model. It is striking that the adjusted R^2 value for the pseudo-second order model (0.99) is significantly lower than the value for the pseudo-first order model (0.9999). This only serves to reinforce the hypothesis that methylene blue adsorption onto the carbon-based adsorbent is following a kinetic mechanism of pseudo-second order. Additionally, the comparatively lower SSR value for pseudo-second order model (2.6348) versus the pseudo-first order model (5.1442), also provides support for the claim that the model captures the true nature of adsorption. The adsorption capacities ($q_{e;cal}$) predicted by the pseudo-second order model closely align with the experimentally observed value ($q_{e;exp}$). The model hypothesizes that the adsorption process occurs through two distinct phases: an initial rapid phase that rapidly achieves equilibrium, followed by a slower, prolonged phase (Zamani & Tabrizi, 2015). The relatively small k_2 value further validates the slow adsorption rate associated with the carbon-based material. The correspondence between model predictions and experimental data is reinforced by the high correlation coefficient R^2 values, which approach unity, and the minimal SSR values, highlighting the robustness of the pseudo-second order model (El-Halwany, 2010; Mriye Aksu & Tezer, 2000). A strong R^2 value (>0.90) supports the model's effectiveness in capturing the adsorption kinetics, while the minor discrepancy (2.63%) between experimental and calculated q_e values, derived from the non-linear plots (Figures 4.12 and 4.13), suggests a close correspondence between theory and empirical observations. The results suggest that the coconut husk derived carbon-based adsorbent

follows the pseudo-second order kinetics for methylene blue adsorption due to this model providing the best fit as indicated by the higher R^2 values and lower SSR hence providing the accuracy of the model in predicting adsorption behaviour. The outcomes of this study are consistent with those reported in earlier research, thereby further substantiating the pseudo-second order mechanism as the prevailing governing principle in this specific adsorption process.

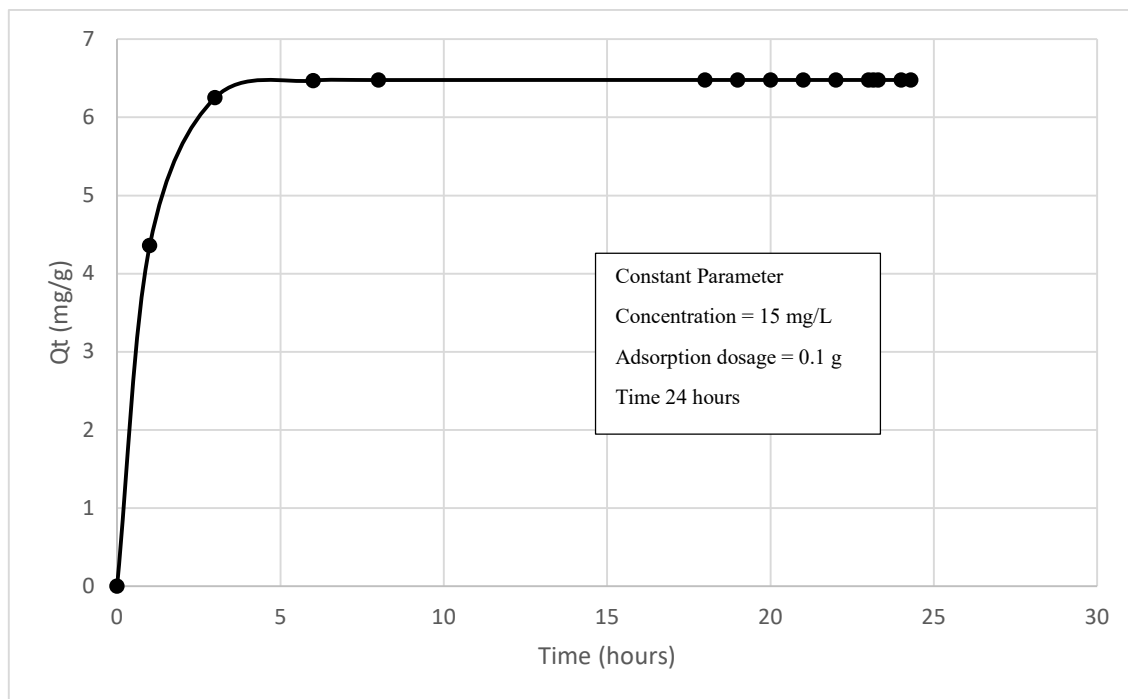


Figure 4.12: Non-linear pseudo-first order kinetic model

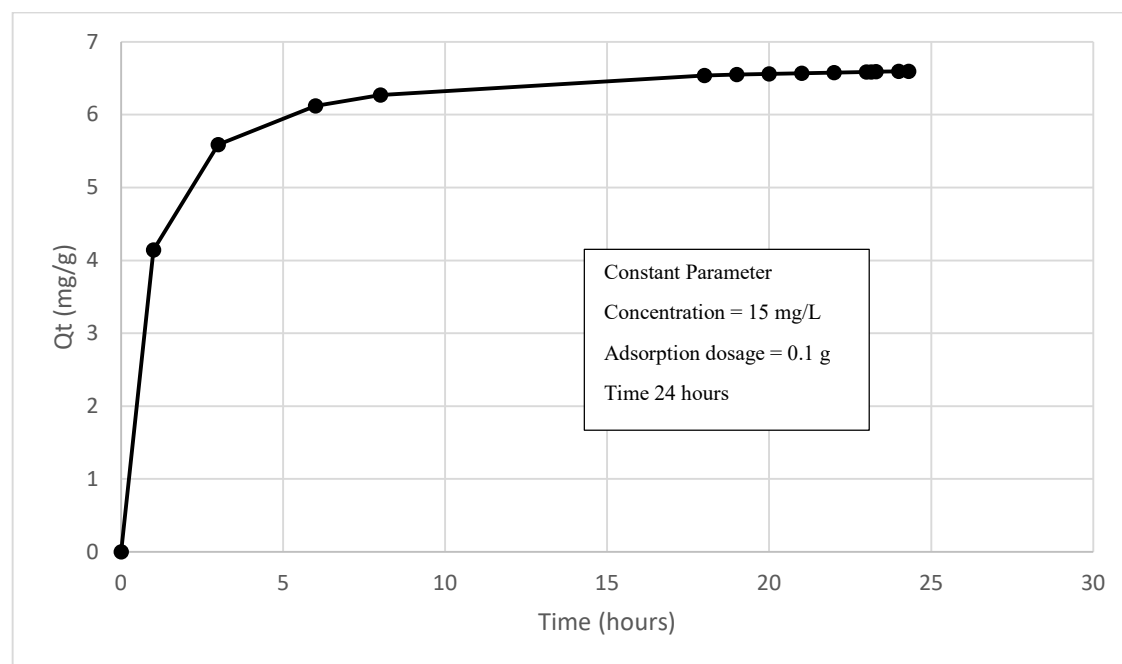


Figure 4.13: Non-linear pseudo-second order kinetic model

Table 4.2: Kinetics parameters for adsorption of methylene blue onto carbon-based material derived from biomass.

Model	Parameter	
Pseudo-first order	Q_t	5.8895
	Q_e	6.4784
	K_1	1.1170
	R^2	0.9999
	SSR (SUM of squared residuals)	5.1442
Pseudo-second order	Q_t	5.8583
	Q_e	6.7684
	K_2	0.2330
	SSR (SUM of squared residuals)	2.6348
	R^2	0.9995

4.8 Adsorption of isotherm study on carbon-based material

The adsorption isotherm models were utilised in experimental data in non-linear regression analysis, employing the Microsoft Excel to estimate isotherm parameters. These parameters were determined based on the non-linear evaluation of the models. The equilibrium adsorption data, obtained under fixed conditions, were analysed using Langmuir, Freundlich and Temkin isotherm models to elucidate the adsorption behaviour of methylene blue onto carbon-based adsorbent. The non-linear plots of Langmuir, Freundlich and Temkin isotherm models, illustrated in Figures 4.14, 4.15 and 4.16, reveal that the

Langmuir model exhibits a superior fit well fit to the experimental data. In contrast, the Freundlich and Temkin models deviate significantly, failing to accurately predict adsorption capacities (q_e) calculated in comparison to the experimentally determined values ($q_{e,exp}$). Nevertheless, it was noted that the adsorption capacity (q_e) determined with the aid of the Langmuir model indeed showed a high degree of fit with the sample adsorption data, demonstrating profound applicability. Furthermore, as evidenced in Table 4.4, the Langmuir model demonstrated the greatest value of the correlation coefficient ($R^2 = 0.96$), suggesting the most accurate representation of the process of adsorption. The Freundlich model yielded an R^2 value of 0.92, while the Temkin model exhibited a slightly lower correlation ($R^2 = 0.88$). The Freundlich constant ($1/n$) was determined to be 0.0778, a value below 1, confirming a normal Langmuir isotherm behaviour (Hameed et al., 2007) and indicating a highly favourable adsorption process. The calculated adsorption capacity (q_{max}) of 14.7334 mg/g closely matched the experimental values obtained from Figure 4.14, further supporting the validity of the Langmuir equation in describing the adsorption equilibrium. The adsorption of methylene blue onto a carbon-based adsorbent occurs via single-layer of exposure on the uniform surface of the carbon-based adsorbent due to the strong fitting of the data obtained to the Langmuir model from the experiments. The result corresponds to earlier investigations reporting analogous adsorption behaviour. Among those is the use of activated carbon derived from coir pith to remove Congo red (Namasivayam & Kavitha, 2002), direct dye adsorption onto sawdust-based activated carbon (Malik, 2004), and methylene blue adsorption onto bamboo-derived activated carbon (Hameed et al., 2007). The separation factor value (3.725×10^{-9}) falls within the range of zero to unity, further affirming the favorable nature of the adsorption process (Namasivayam & Kavitha, 2002; Hameed et al., 2007; Malik, 2004). The quality of the model fit was assessed using statistical

parameters such as R^2 and the sum of squared residuals (SSR). The Langmuir model demonstrated the lowest possible SSR value (1) and the highest possible R^2 value (0.96), thereby confirming its superiority in accurately describing equilibrium adsorption behavior. These findings confirm that the removal of methylene blue occurs via monolayer adsorption on structurally homogeneous carbon-based adsorbent surface.

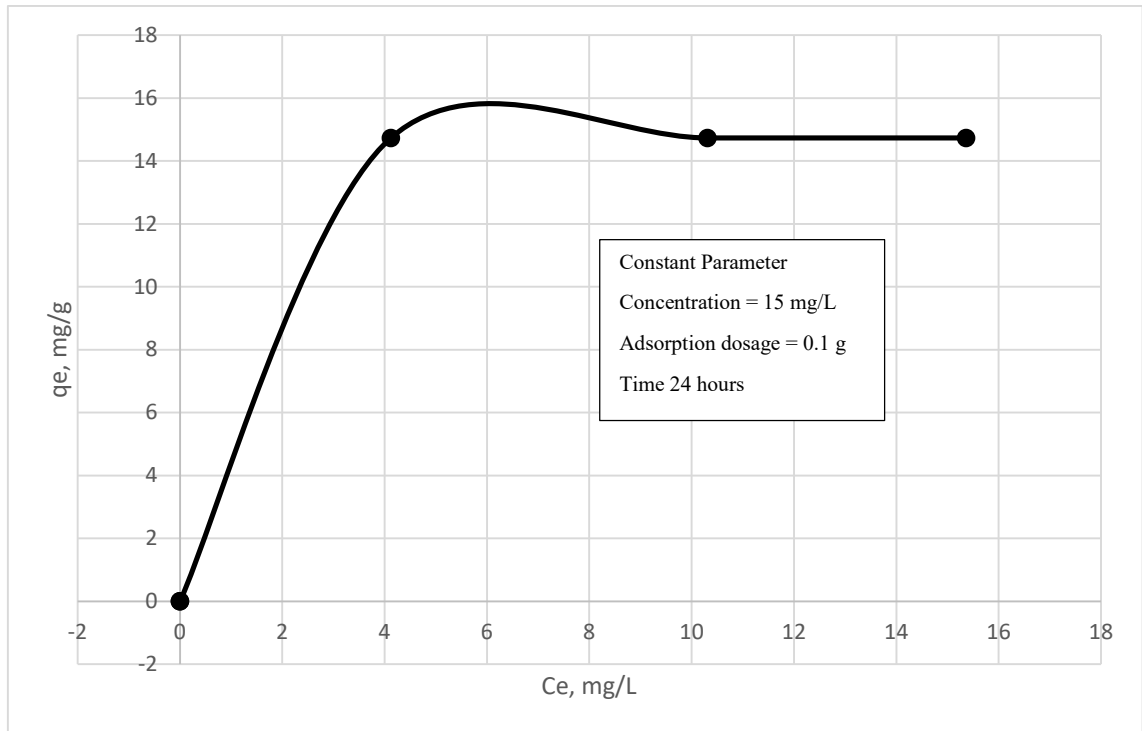


Figure 4.14: The fittings of experimental data by using Langmuir model

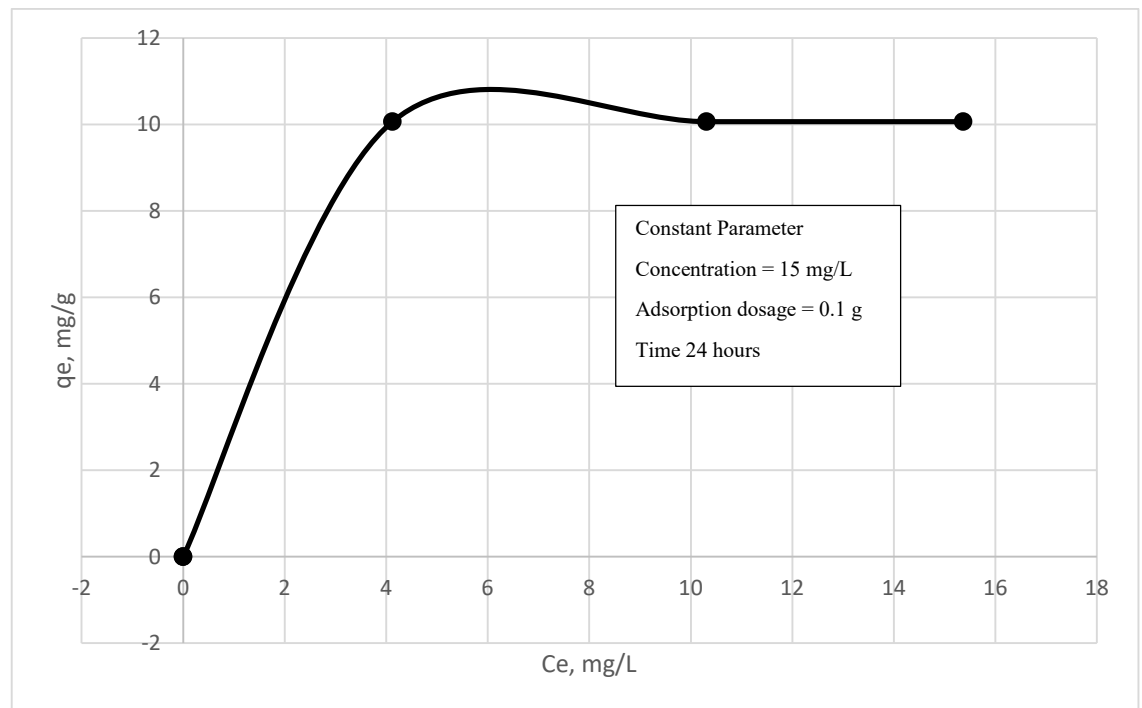


Figure 4.15: The fittings of experimental data by using Freundlich

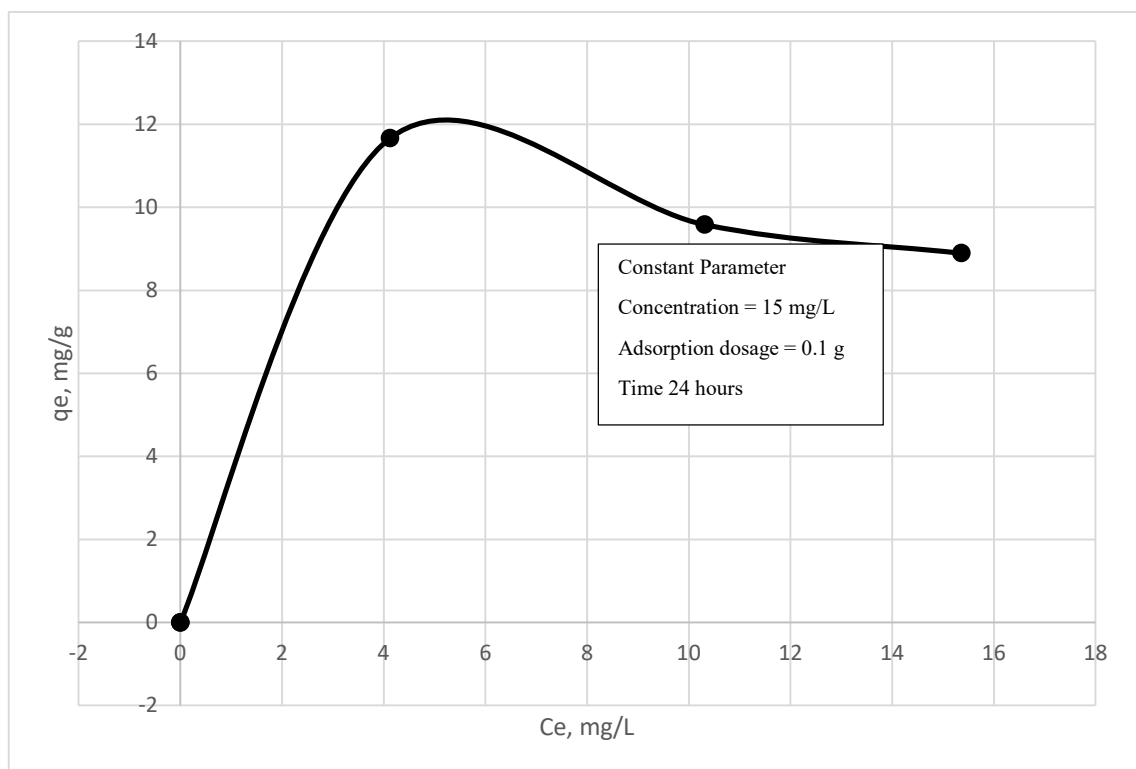


Figure 4.16: The fittings of experimental data by using Temkin model

Table 4.3: The parameter of the isotherm models for methylene blue adsorption

Isotherm model	Parameter	Value
Langmuir	$q_{max} (mg g^{-1})$	14.7343
	$K_L (L mg^{-1})$	536871
	R^2	0.96
	SSR	1
Freundlich	K_F	10.4728
	$1/n$	0.0778
	R^2	0.9286
	SSR	125.98

Table 4.3:

Continued

Temkin	$K_T (L\ mg^{-1})$	16.5372
	$B\ (J/mol)$	50.3450
	R^2	0.9280
	SSR	126.1828

4.9 Temperature and thermodynamic of adsorption study

The study studied the impact of temperature on the adsorption of methylene blue onto carbon-based material. All the solutions with specific concentrations (15 mg/L) of methylene blue were prepared at different temperature (25, 35, 55, 65, and 85 °C) as shown in Figure 4.17. Research results indicate that adsorption capacity of methylene blue on carbon-based material increased as temperature elevated among all concentrations, indicating a spontaneous endothermic process. The observed behaviour can be attributed to the chemical potential, solubility, and increasing thermal energy of dye molecules with increasing temperature, as explained by (Kuang et al., 2020). Moreover, the temperature exerted an influence on the pore structure of carbon-based material.

Further insights into the temperature effect and sorption mechanism were gained through an analysis of thermodynamics of adsorption. The energy perspective was taken for analysing the thermodynamics of adsorption of carbon-based material. The utilization of adsorption thermodynamics in the study of adsorbates driving force facilitated the assessment of the spontaneity of the process. The thermodynamic parameters are changes in

enthalpy (ΔH), change of entropy (ΔS), and change of Gibbs free energy change (ΔG) were crucial in this analysis.

At temperatures of 298K, 308K, 328K, 338K, and 358K, the ΔG values were 1.1369, 0.4779, -0.1548, -0.3823, and -1.6676 kJ/mol respectively. These values indicated a transition from a nonspontaneous to a spontaneous reaction for the removal of methylene blue as the temperature rose. The reaction takes place autonomously when temperature increases. The values of enthalpy, ΔH and entropy were determined as 13.873 kJ/mol and 42.916J/mol.K, respectively. These results suggest that the adsorption processes of adsorption were endothermic and accompanied by increase of disorder. Table 4.5 showed the results in detail.

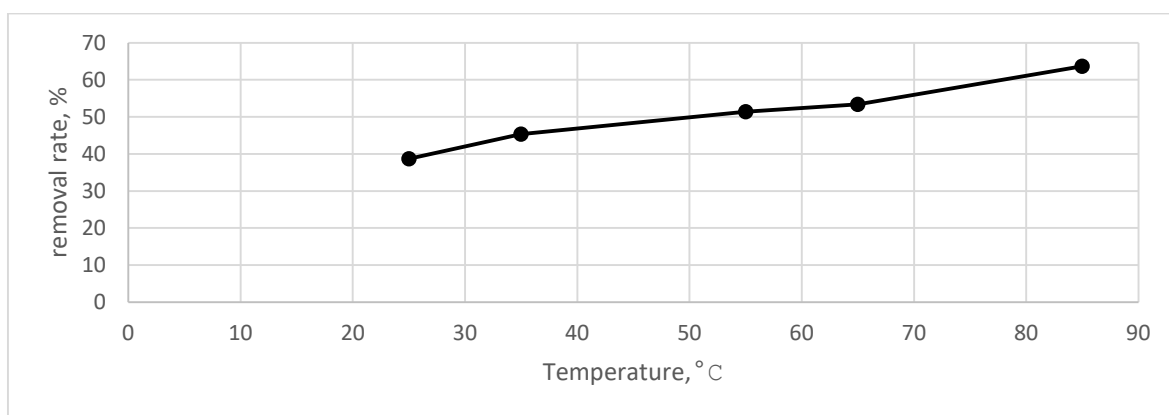


Figure 4.17: Effect of the temperature for removal of methylene blue on carbon-based material

Table 4.4: Thermodynamic parameters for removal of methylene blue on carbon-based material

Temperature (K)	298	308	328	338	358
$\Delta G^\circ(kJ/mol)$	1.1369	0.4779	-0.1548	-0.3823	-1.6676
$\Delta S^\circ(kJ/(K mol))$	42.916				

Table 4.4 continued

$\Delta H^\circ(kJ/mol)$	13.873
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CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The current study explored the effectiveness of a carbon-based materials, with a focus on its application in removing methylene blue from aqueous solutions. The key findings drawn from this investigation are as follows: Characterization analyses revealed a well-established porous structure with a diverse range of pore dimensions, supporting the material's adsorption capability. Furthermore, the elemental composition, as determined by energy-dispersive X-ray (EDX) analysis, revealed that the carbon-based material consists of 71.55% carbon, 18.55% oxygen, 2.31% chlorine, and 7.59% iron. Furthermore, Brunauer-Emmett-Teller (BET) surface area analysis indicated a specific surface area of $68.443 \text{ m}^2/\text{g}$, thereby highlighting its suitability for adsorption applications. Adsorption equilibrium was established within 24 hours, thereby emphasizing the necessity of sufficient contact time for optimal adsorption efficiency. Kinetic investigations demonstrated that the adsorption of the carbon-based material in removal methylene blue was a relatively slow adsorption process, aligning with the pseudo-second-order kinetic model. This suggests that the adsorption mechanism is predominantly governed by chemisorption, involving strong interactions between the dye molecules and the adsorbent surface. The extent of dye adsorption was positively influenced by increasing initial solution pH, dye concentration, contact time, adsorbent dosage, and system temperature. However, at excessively high initial dye concentrations, removal efficiency declined due to the saturation of available adsorption sites. Notably, the carbon-based material exhibited excellent performance in capturing

methylene blue at lower concentrations, reinforcing its applicability for real-world wastewater treatment. The equilibrium adsorption data exhibited a strong correlation with the Langmuir isotherm model, yielding the highest monolayer adsorption capability about 14.7343 mg/g. The dimensionless separation factor (R_L) further confirmed the feasibility and effectiveness of this material for methylene blue removal. Thermodynamic evaluations conducted across five different temperatures provided deeper insights into the adsorption mechanisms. The positive enthalpy changes (ΔH°) and positive entropy change (ΔS°) observed suggest that is endothermic in this adsorption process and characterized by a rise in disorder at the interface between solids and liquids. Furthermore, the transition from positive to negative Gibbs free energy change (ΔG°) signifies that the adsorption is not only spontaneous but also irreversible under the studied conditions. In summary, this research highlights the viability of coconut husk- derived carbon-based material to provide an effective, affordable, and ecologically sustainable adsorption material to remove methylene blue. The favourable adsorption capacity, renewable nature, and economic feasibility of this biomaterial suggest that it could serve as a potential substitute for traditional adsorbents in application involving wastewater treatment.

5.2 Recommendations

It is recommended that the carbon-based material derived from coconut husk be used to mix with other materials to form a composite for further improving the properties of the carbon-based material. The oxidizing agent in the project can be modified or mixed with another oxidizing agent to improve the functional groups in treating the heavy metals. To further enhance the optimization of the carbon-based material, a response surface methodology can be adopted to design and run the optimization experiments. In addition,

the carbon-based material can be used in other applications such as conductive material in energy industry.

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APPENDDICES

Appendix A: Calculation of thermodynamic

The calculation of thermodynamic section was measured using excel solver. The addition information will be shown in Table 1 as well as the equation used.

$$\Delta G^{\circ} = -RT \ln K_c$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$

$$K_c = \frac{C_a}{C_e}$$

Where, K_c = coefficient of distribution for adsorption, C_a ($mg L^{-1}$) = dye adsorbed by unit mass of adsorbent, R = universal gas constant ($8.314 J mol^{-1} K^{-1}$) and T (K) = absolute operational temperature. ΔH° and ΔS° were determined from the slope and intercept of a linear plot of ΔG° VS. T respectively.

Temp °C	T Kelvin	1/T	K_c	$\ln K_c$	R	ΔG°	ΔG°
25	298	0.003355705	0.632005081	-0.45886	8.314	1136.853	1.136853
35	308	0.003246753	0.829758867	-0.18662	8.314	477.8804	0.47788
55	328	0.00304878	1.058393689	0.056752	8.314	-154.763	-0.15476
65	338	0.00295858	1.145734966	0.136046	8.314	-382.308	-0.38231
85	358	0.002793296	1.751129576	0.560261	8.314	-1667.57	-1.66757

Intercept	slop	R square	R	ΔH°		ΔS°
5.1619	-1668.61	0.9706	8.314	13872.79	13.87279	42.91604