



Faculty of Engineering

**Synthesis of Sago Bark-Derived Magnetic-Activated Carbon for
Methylene Blue Removal**

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Synthesis of Sago Bark-Derived Magnetic-Activated Carbon for Methylene Blue 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

While adsorption is recognized as an effective water treatment method, the high cost associated with conventional adsorbents hinders its feasibility for widespread applications. Therefore, this study aims to synthesis and characterise magnetic-activated carbon derived from sago bark (SBMAC), an abundant agriculture waste, as a low-cost adsorbent for the removal of methylene blue dye from an aqueous solution. Beforehand, the optimal SBMAC preparation parameters were determined using the response surface methodology Box-Behnken Design (BBD) via the Stat-Ease Design Expert software. The response surface methodology BBD revealed that the optimal preparation parameters for SBMAC were an impregnation ratio of 1.5, a pyrolysis temperature of 700°C, and a heating time of 60 minutes. By employing the optimal preparation parameters, SBMAC was prepared through single-stage pyrolysis and impregnated with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as magnetic media and KOH as an activating agent. The sago bark powder (SBP), SBMAC, and SBMAC after dye adsorption (SBMAC2) were characterised using BET, SEM-EDX, and FTIR analyses. Furthermore, The BET analysis of SBMAC reveals a specific surface area of 849.906 m^2/g and a total pore volume of 2.47 cm^3/g , 30 times higher than SBP and decreasing after adsorption. The FTIR analysis of SBMAC and SBMAC2 indicates the presence of the stretching vibration of Fe-O, which is absent in SBP. Additionally, stronger O-H peak intensities and the presence of C-Cl band following methylene blue adsorption indicate the occurrence of methylene blue adsorption. The SEM analysis displays a granular texture for SBP and SBMAC, although SBMAC exhibits fewer visible pores than SBP. Additionally, EDX analysis of SBP reveals a high percentage of carbon and oxygen, whereas SBMAC and SBMAC2 have high percentages of carbon, oxygen, and iron elements. The SBMAC was employed in batch adsorption experiments to evaluate

adsorption kinetics, isotherms, the effect of temperature and adsorption thermodynamics, the effect of adsorbent dosage, and the pH_{PZC} and the effects of pH. The batch kinetics experiments were conducted at four distinct dye concentrations (100 mg/L, 200 mg/L, 300 mg/L, and 500 mg/L). The results indicate that the highest initial dye concentration required the longest duration to reach equilibrium, in contrast to the lower concentrations. Furthermore, the adsorption of all four initial concentrations exhibited the best fit with the pseudo-second-order (PSO) kinetic model, displaying R^2 values exceeding 0.998, in contrast to the pseudo-first-order (PFO) model. Notably, the kinetic adsorption data did not align with the intraparticle diffusion model (ID), indicating that multiple processes influence the dye adsorption onto SBMAC. In the context of adsorption isotherms, the model that fits best is the Freundlich isotherm model, exhibiting an R^2 value of 0.9662 along with a maximum adsorption capacity (q_{max}) of 1655.05 mg/g. Meanwhile, for the effect of temperature and adsorption thermodynamics, the highest adsorption capacity was attained at the lowest temperature of 30°C, and the adsorption process was found to be exothermic. For the effect of adsorbent dosage, the most optimal adsorbent dosage was observed at 1.0 g/L for the removal of dye. For pH_{PZC} and the effect of pH, the pH_{PZC} of the adsorption was calculated at pH 6.74 and the highest adsorption capacity was obtained at the initial pH 11. In conclusion, SBMAC was successfully prepared from sago bark having a high-adsorption capacity adsorbent for the removal of methylene blue dye applications.

Keywords: Sago bark, magnetic activated carbon, adsorption, methylene blue, process optimisation

Sintesis karbon diaktifkan magnetik daripada kulit pokok sagu untuk penyingkiran biru metilena

ABSTRAK

Walaupun penjerapan dikenali sebagai kaedah rawatan air yang berkesan, kos tinggi yang berkait dengan penjerap konvensional menghalang kebolehan untuk aplikasi yang meluas. Oleh itu, kajian ini bertujuan untuk menghasilkan dan mengkaraktirikan karbon aktif magnetik yang berasal dari kulit sagu (SBMAC), sisa pertanian yang berlebihan, sebagai penjerap kos rendah untuk penyingkiran pewarna metilena biru dari larutan akuas. Sebelum itu, parameter penyediaan SBMAC yang optimum ditentukan menggunakan kaedah response surface methodology Box-Behnken Design (BBD) melalui perisian Stat-Ease Design Expert. Kaedah response surface methodology BBD mendedahkan bahawa parameter penyediaan optimum untuk SBMAC adalah nisbah pengimpregnasi 1.5, suhu pirolisis 700°C, dan masa pemanasan 60 minit. Dengan menggunakan parameter penyediaan optimum ini, SBMAC telah dihasilkan melalui pirolisis satu peringkat dan diimpregnasi dengan $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ dan $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ sebagai media magnetik dan KOH sebagai agen pengaktifan. SBMAC digunakan dalam eksperimen penjerapan kelompok untuk menilai kinetik penjerapan, isoterma, kesan suhu dan termodinamik penjerapan, kesan dos penjerap, pH_{PZC} , dan kesan pH. Serbuk kulit sagu (SBP), SBMAC, dan SBMAC selepas penjerapan pewarna (SBMAC2) dikarakteristikkan menggunakan analisis BET, SEM-EDX, dan FTIR. Selanjutnya, analisis BET SBMAC mendedahkan kawasan permukaan khas sebanyak 849.906 m²/g dan isipadu liang keseluruhan sebanyak 2.47 cm³/g, 30 kali lebih tinggi daripada SBP dan berkurang selepas penjerapan. Analisis FTIR SBMAC dan SBMAC2 menunjukkan kehadiran getaran regangan Fe-O, yang tidak hadir dalam SBP. Selain itu, intensiti puncak O-H yang lebih

kuat dan kehadiran jalur C-Cl selepas penjerapan metilena biru menunjukkan penjerapan metilena biru. Analisis SEM menunjukkan tekstur butiran bagi SBP dan SBMAC, walaupun SBMAC menunjukkan liang yang kurang kelihatan berbanding SBP. Selain itu, analisis EDX SBP mendedahkan peratusan tinggi karbon dan oksigen, manakala SBMAC dan SBMAC2 mempunyai peratusan tinggi unsur karbon, oksigen, dan unsur besi. Eksperimen kinetik kelompok dijalankan pada empat kepekatan pewarna yang berbeza (100 mg/L, 200 mg/L, 300 mg/L, dan 500 mg/L). Keputusan menunjukkan bahawa kepekatan pewarna awal tertinggi memerlukan masa paling lama untuk mencapai keseimbangan, berbeza dengan kepekatan yang lebih rendah. Selain itu, penjerapan semua empat kepekatan awal menunjukkan kesesuaian terbaik dengan model kinetik pseudo-second-order (PSO), dengan nilai R^2 melebihi 0.998, berbeza dengan model pseudo-first-order (PFO). Perlu diperhatikan bahawa data kinetik penjerapan tidak selaras dengan model difusi intrapartikel (ID), menunjukkan bahawa terdapat pelbagai proses yang mempengaruhi penjerapan pewarna ke SBMAC. Dalam konteks isoterma penjerapan, model yang paling sesuai adalah model isoterma Freundlich, dengan nilai R^2 sebanyak 0.9662 dan kapasiti penjerapan maksimum (q_{max}) sebanyak 1655.05 mg/g. Sementara itu, bagi kesan suhu dan termodinamik penjerapan, kapasiti penjerapan tertinggi dicapai pada suhu terendah 30°C, dan proses penjerapan didapati bersifat eksotermik. Bagi kesan dos penjerap, dos penjerap optimum yang paling berkesan diperoleh pada 1.0 g/L untuk penyingkiran pewarna. Bagi pH_{PZC} dan kesan pH, pH_{PZC} penjerapan telah dikira pada pH 6.74 dan kapasiti penjerapan tertinggi diperoleh pada pH awal 11. Kesimpulannya, SBMAC berjaya dihasilkan dari kulit sagu dengan kapasiti penjerapan yang tinggi untuk aplikasi penyingkiran pewarna metilena biru.

Kata kunci: Kulit pokok sagu, karbon diaktifkan magnetik, penjerapan, biru metilena, pengoptimuman proses

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
BBD	Box-Behnken Design
BET	Brunauer-Emmet-Teller
DOE	Design of experiment
DR	Dubinin-Radushkevich
EDX	Energy dispersive X-ray
FTIR	Fourier transform infrared
ID	Intraparticle diffusion
MAC	Magnetic activated carbon
PFO	Pseudo-first-order
PSO	Pseudo-second-order
RSM	Response surface methodology
SBMAC	Sago bark magnetic activated carbon
SBMAC2	Sago bark magnetic activated carbon after adsorption
SBP	Sago bark powder
SEM	Surface electron microscopy
TGA	Thermogravimetric
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Study Background

A significant amount of research has been conducted to develop a high-efficiency and cost-effective adsorbent that is used for the adsorption of toxic pollutants in wastewater. Of all adsorbents available in the industry, activated carbon has the highest potential due to its high adsorption capacity, high porous structure, and high efficiency in liquid-phase contaminant removal (Wang et al., 2023). Despite that, the application of activated carbon in the adsorption system needs to be accompanied by a filtration system for the separation and recovery process of adsorbent from water bodies causing the process to be expensive, time-consuming, and inefficient (Ling, 2022). Therefore, the use of activated carbon is unfitting for industrial-scale applications.

Consequently, a growing amount of research is being focused on the low-cost recovery of powdered activated carbon from water bodies and magnetisation of activated carbon is one of the promising innovations that can facilitate the issue (Moosavi et al., 2020). The magnetisation of activated carbon is simply incorporating magnetic particles onto the porous structure of activated carbon which enables an easier recovery of activated carbon from the aqueous medium (Moosavi et al., 2020). Thus, the application of activated carbon as a low-cost and high-efficiency adsorbent for industrial scale is feasible by associating magnetic particles with the activated carbon.

In this study, agriculture waste material that is used to prepare a novel magnetic activated carbon is sago bark from a sago palm tree. Sago bark is a waste generated from sago starch production along with sago pith. In Malaysia, sago starch is mainly exported

from Sarawak to Peninsular Malaysia and Japan. Sarawak is recognized as the largest exporter of sago starch in Malaysia, catering to both domestic and international markets, with a notable export destination being Japan (Ling, 2022). Sago palm scientifically known as *Metroxylon sago* is one superior type of starch type crop which have a high production capacity compared to cassava, corn, and rice with production of 20 to 25 tons of starch produced per harvest for a year (Amin et al., 2019). The production of one ton of dried sago starch results in the generation of approximately half a ton of sago bark waste. This waste is often either incinerated or improperly discarded into nearby rivers, posing environmental hazards (Tan et al., 2021). Thus, converting sago bark into low-cost and high-efficiency activated carbon will add value to it as well solve as waste management issues.

The primary aim of this study is to produce magnetic activated carbon from sago waste, specifically sago bark, for its potential application as an adsorbent in wastewater treatment for dye removal. While numerous studies have focused on developing magnetic-activated carbon using various agricultural wastes, there is currently no research available on the production of magnetic-activated carbon utilizing sago bark.

1.2 Problem Statement

Excessive waste production as a by-product of agricultural activities has become a growing concern worldwide. A study published in the Chemical Engineering Journal Advances by Karić et al. (2022) reveals that approximately 998 million tonnes of agricultural waste are generated each year. Agriculture significantly contributes to climate change, accounting for 21% of all greenhouse gas emissions, adversely affecting the environment due to the lack of an effective waste management system. One specific type of agricultural waste, sago bark, poses a significant challenge due to its large volume and

the environmental risks associated with its disposal. The production of one ton of dried sago starch results in the generation of approximately half a ton of sago bark waste. This waste is often either incinerated or improperly discarded into nearby rivers, posing environmental hazards (Tan et al., 2021). While waste treatment is a potential solution, it can be prohibitively expensive for small agricultural business owners. However, there is a promising prospect for addressing this problem by converting agricultural waste, including sago bark, into valuable resources. This approach not only promotes environmental sustainability but also contributes to the agricultural economy. By harnessing the potential of agricultural waste, innovative strategies can be employed to mitigate environmental impacts and foster a more sustainable future.

On the contrary, clean water is one of the most basic human needs, and the United Nations has listed it as a Sustainable Development Goal (SDG) under Goal 6: Clean Water and Sanitation, which assures access to safe water, sanitation, and hygiene (Warner et al., 2022). In order to avoid the spread of water-borne diseases, every source of raw water typically undergoes a sequence of water treatment systems prior to distribution to consumers to remove any contaminants. One of the contaminants that has garnered concern globally is dye. These synthetic compounds are hazardous, persistent, and carcinogenic, which makes their presence in waterbodies a serious environmental threat (Oladoye et al., 2022). Due to the rapid rate of industrialization and population growth, the usage of dyes in various production industries (cosmetics, pharmaceuticals, textiles, etc.) has increased significantly. The effects of increased dyes in wastewater include visual pollution, which reduces the aesthetic appeal of water resources, and a decrease in light penetration into water bodies, which affect the aquatic ecosystems and hinder photosynthesis (Sasidharan et al., 2021). Efficient dye removal is important to prevent

water pollution, safeguard public health, and maintain ecological balance. One effective method to remove dye from wastewater is by the adsorption process using adsorbent.

Adsorption techniques are high-efficiency tertiary wastewater treatment methods that are typically expensive due to the type of adsorbent used for the process. Due to its large surface area, activated carbon made from agricultural waste is known as a low-cost and high-performance adsorbent. However, the application of activated carbon for the removal of pollutants in an industrial setting is challenging and uneconomical due to its difficulty in separating the activated carbon from the water bodies. Thus, a novel magnetic activated carbon will be prepared in this project using sago bark (agricultural waste) for the removal of dye in wastewater.

1.3 Research Gap

There has been inadequate research on the preparation of magnetic activated carbon from sago bark using KOH as an activating agent and an association of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ for iron impregnation. While there have been studies on the synthesis of activated carbon from sago bark using different activation agents (Erabee et al., 2017; Togibasa et al., 2021), there has been a research gap in the impregnation of iron on sago bark-derived magnetic activated carbon for the removal of methylene blue dye.

Furthermore, there has been a lack of research on the optimisation of the iron impregnation ratio on sago bark-derived magnetic activated carbon for the elimination of methylene blue dye using Response Surface Methodology (RSM) Box-Behnken design, including the optimisation of pyrolysis temperature and heating time. There is a research gap in the optimisation of the impregnation ratio of iron on sago bark-derived magnetic activated carbon for the removal of methylene blue dye using RSM Box-Behnken design, even though RSM has been used in numerous studies for optimisation purposes, including

the optimisation of magnetic-activated carbon derived from marine microalgae (Jung et al., 2019), cotton waste (Xu et al., 2018) and oil palm fibre (Marsin et al., 2020) preparation parameters. Additional studies could investigate using the RSM Box-Behnken design to optimise the iron impregnation ratio on sago bark-derived magnetic activated carbon, as well as the pyrolysis temperature and heating time, and evaluating the performance of the optimised adsorbent for methylene blue dye removal.

Despite studies on the preparation of activated carbon for dye adsorption from waste biomass are available, the precise adsorption mechanism and effectiveness of MAC made from sago bark have not been extensively explored. Therefore, further studies could explore the adsorption behaviour of MAC from sago bark towards methylene blue dye.

1.4 Objectives

The main aim of this study is to produce magnetic-activated carbon sago bark, for its potential application as an adsorbent in wastewater treatment for methylene blue dye removal. The specific objectives of this research are as stated below:

- i. To synthesis and optimise the sago bark magnetic-activated carbon for methylene blue dye removal;
- ii. To characterise the sago bark magnetic-activated carbon using instrumental analysis (BET, SEM-EDX and FTIR analysis); and
- iii. To evaluate the adsorption behaviours of the sago bark magnetic activated carbon on dye using batch adsorption.

1.5 Hypothesis

The hypotheses for this study are:

- i. Sago bark magnetic-activated carbon will be effectively prepared using single-stage pyrolysis, and iron will be successfully impregnated employing the impregnation method.
- ii. Prepared sago bark magnetic activated carbon will have a high porosity and an abundance of functional groups.
- iii. The adsorption behaviours of sago bark magnetic activated carbon on dye would show the high capacity and efficiency of the prepared adsorbent.

1.6 Scope of study

The scope of the study for this research focuses on the preparation and characterisation of magnetic activated carbon using sago bark as a precursor via single-stage pyrolysis, in which sago bark was first impregnated with Fe^{2+} and Fe^{3+} and chemically activated using KOH before pyrolysis. Response surface methodology (RSM) with Box-Behnken design is applied for optimisation studies to identify the optimal values of pyrolysis temperature (400-700°C), impregnation ratio of magnetic materials (0-1.5) and heating time (60-120 mins) for preparation of sago bark magnetic activated carbon. Then, the adsorbent is characterised using BET, SEM-EDX, FTIR analysis. The adsorption behaviours of sago bark magnetic activated carbon are determined through batch adsorption experiments, assessing its performance in removing methylene blue dye using kinetic and isotherm models. The kinetic study is limited to initial concentration of 100-500 mg/L with 1440 minutes contact times. Meanwhile, isotherm study is limited to initial concentration of 80-500 mg/L with 1440 minutes contact times.

CHAPTER 2

LITERATURE REVIEW

2.1 Sago Palm (*Metroxylon sago*)

The Sago palm, scientifically referred to as *Metroxylon sago*, is a unique starch crop known for its exceptional production capacity, surpassing that of cassava, corn, and rice. It yields approximately 20 to 25 tons of starch per harvest annually (Amin et al., 2019). One mature sago palm tree can generate between 100 and 550 kg of sago starch, producing roughly 60 million tons annually in southeast Asia (Singh et al., 2011). In Malaysia, sago starch is mainly exported from Sarawak to Peninsular Malaysia and Japan. Sarawak is known to be Malaysia's biggest exporter of sago starch within Malaysia and overseas, particularly in Japan. 51.47% of sago starch was exported to Peninsular Malaysia, while 35.47% was exported to Japan. In 2020, it was reported that Sarawak had exported 37,884 metric tons of sago starch worth RM78.29 million. Currently, the sago industry in Sarawak is dominated by small businesses, around 92% of the total estimated sago planted area of 32,329 hectares (Kavitha et al., 2023).

Sago starch, the main product of sago palms, is consumed by locals as a substitute for rice or processed further to make various culinary products, including noodles and regional favourites (tebaloi and sago pearls). Sago starch is also used extensively outside the food industries, particularly in the paper, wood, and textile sectors (Tie et al., 2008). The sago palm tree is used for not only its starch but also its fibre for rumen fermentation, its pith as animal feed, its fronds in the pulp and paper industry, and its trunk as an excellent building material, compost, and energy resource (Abd-Aziz, 2002). However, these byproducts of sago palm trees are not fully utilized, resulting in waste after sago

starch production. The waste accumulates over time, as the amount of waste left unutilized after each production cycle only increases, posing a significant problem for the mills due to the lack of value associated with the waste. This waste, which lacks any practical applications, is later improperly disposed of as there is no appropriate rules imposed by the local government on how to deal with the waste produced by sago starch mills, which results in a worry for the environment on the part of the local population.

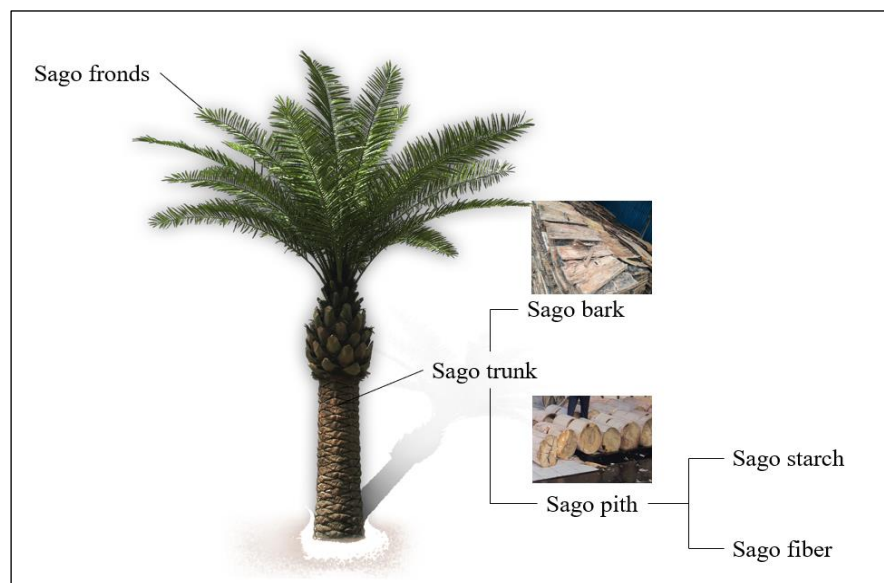


Figure 2.1: Sago palm tree and the by-products of sago trunk

Sago starch production generates three types of waste: sago bark, sago fibre, and wastewater. Figure 2.1 shows a sago palm tree and the byproducts of the subsequent parts. The debarking process of a sago palm trunk yields sago bark, while the extraction of sago starch generates sago fibers. Additionally, the washing of sago starch leads to the production of wastewater. Sago bark and fibers are categorised as solid waste, whereas the discharge of water from sago starch production is referred to as wastewater. In a single day, the processing of approximately 600 sago palm logs results in the production of 5.6 tons of woody bark, 238 tons of wastewater, and 7.1 tons of fibrous pith residue (Ngaini et al., 2014). All these waste products are either incinerated or dumped in a nearby river,

particularly polluting the river and the air, which will result in significant environmental problems in the future.

Sago waste is classified as lignocellulosic biomass as it comprises polysaccharides (cellulose and hemi-cellulose) and an aromatic polymer (lignin). The utilization of lignocellulosic biomass holds considerable promise as a viable substitute for fossil fuels in the production of second-generation biofuels as well as bio-based chemicals and materials (Zoghلامي & Paës, 2019). Thus, numerous studies have been conducted, particularly on sago bark, to fully utilize and add value to the waste product from the production of sago starch.



Figure 2.2: Waste management of sago bark at local sago mill

2.1.1 Sago Bark

Sago bark is the outermost layer of the sago trunk that is discarded during the debarking process to acquire the sago pith for starch extraction. Every ton of sago starch generates approximately 0.75 tons of sago bark as solid waste, and 85% is left unutilized (Wahi et al., 2017). Due to the high acidity of sago bark, only 15% of 20,000 tons of sago bark produced each year was employed as timber fuel for the drying process of the starch (Wahi et al., 2014). The high acidity of sago bark will induce corrosion and buildup within the furnace, resulting in damage in the future. The sago bark that is not put to use will

either be burned, thrown away into the nearby river, or left at the mill area to naturally degrade. All of these waste management methods are not sustainable in the long run. Discarding excessive sago bark into the river will reduce the river's depth, unauthorized burning will pollute the air, and keeping sago bark waste at the mill will take up space and produce an unpleasant smell and sight. Figure 2.2 shows images of sago bark waste (a) dumped at the river's jetty and an abundance of sago bark waste (b) kept at the mill site. In light of this, numerous investigations have been conducted to understand sago bark's nature and possible applications.

Characterisation of sago bark is a crucial study that needs to be conducted to thoroughly understand its characteristics before using it in subsequent studies. In general, few characterisation studies, such as the proximate analysis, ultimate analysis, chemical composition, surface morphology, surface elemental composition, functional group, and crystallinity, have been employed to evaluate lignocellulosic biomass further (Onokwai et al., 2022). Biomass proximate analysis is crucial for understanding how much energy can be obtained from the material, as it reveals how much of the biomass is gaseous (volatile matter), solid (fixed carbon), and inorganic waste (ash). Biomass with a high percentage of fixed carbon will yield a high amount of biochar. In contrast, biomass with a high content of ash and volatile matter will yield a high amount of gas generation and low biochar production (Nunes et al., 2018). According to Jha and Dass (2020), less than 5% of ash content is considered low, 5-10% is considered medium, and more than 10% is considered high. Based on the data in Table 2.1, sago bark biomass can be classified as low ash biomass as the ash content calculated is lower than 5%.

Moreover, an ultimate analysis was conducted to ascertain the elemental composition of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) in

biomass. A high percentage of carbon and oxygen in biomass suggests it is favourable for energy generation, while a low percentage of nitrogen implies that NO_x emissions can be negligible (Jha & Dass, 2020). According to Table 2.1, sago bark's suitability for energy generation can be inferred from its carbon and oxygen percentage greater than 90%. Since nitrogen is less than 1.5%, NO_x formation will be in traces. Table 2.1 presents the proximate and ultimate analysis of sago bark conducted by Siruru et al. (2019), Rambli et al. (2018), Erabee et al. (2017), and Wahi et al. (2014).

Table 2.1: Proximate and ultimate analysis of sago bark from three different study

	Siruru et al. (2019)	Rambli et al. (2018)	Erahee et al. (2017)	Wahi et al. (2014)
Proximate analysis (wt%)				
Moisture content	4.9	13.9	9.0	10.9
Volatile matter	81.4	73.6	-	77.8
Ash	1.3	4.6	1.5	3.4
Fixed carbon	18.7	7.9	-	12.9
Ultimate analysis (wt%)				
C	44.6	35.7	45.2	42.4
H	6.4	6.7	6.3	5.6
O	47.8	57.2	48.5	50.6
N	0.03	0.2	0.0	1.4
S	0.1	0.2	0.01	-

The elemental chemical composition analysis was conducted to determine the composition of lignocellulosic biomass, which encompasses cellulose, hemicellulose, and lignin. Table 2.2 displays the chemical composition of sago bark, as determined by Erabee et al. (2017), and Siruru et al. (2019). According to Siruru et al. (2019), the concentration of lignin in lignocellulosic biomass plays a crucial role in char generation, as a higher lignin content enhances char yield for the production of activated carbon due to the

formation of more aromatic groups. Lignin percentages in sago bark have been determined to be 23.3% (Erabee et al., 2017) and 29.4% (Siruru et al., 2019), an appropriate quantity of lignin for char production. Based on the data from Table 2.2, the amount of cellulose in sago bark is the highest, followed by lignin and hemicellulose.

Table 2.2: Chemical composition of sago bark

Chemical composition (%)	Erabee et al. (2017)	Siruru et al. (2019)
Cellulose	44.13	44.0
Hemicellulose	21.09	22.8
Lignin	23.30	29.4

Surface morphology is a study of the biomass's surface structure and shape, which was examined using Scanning Electron Microscopy (SEM). The determination of surface elemental composition, commonly performed using Energy Dispersive X-Ray (EDX) analysis, is frequently associated with this type of analysis. Both analysis is done to study the surface characteristics of biomass. Surface morphology is a straightforward investigation in which the surface of the biomass is examined to see whether pores and chemical elements are present, which can be confirmed using the information from the EDX. Figure 2.3 depicts SEM images of raw sago bark and activated sago bark carbon

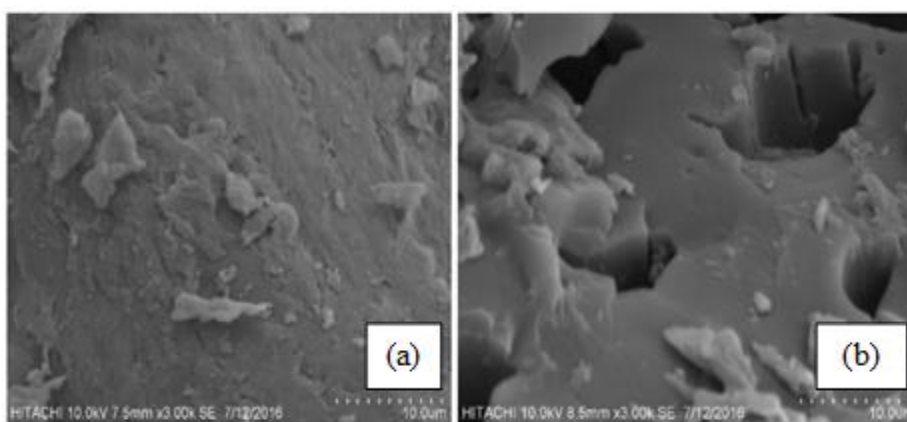


Figure 2.3: SEM images of (a) sago bark and (b) sago bark activated carbon (Erabee et al., 2017)

examined by Erabee et al. (2017), who found the structure of sago bark before carbonization to be rigid and non-porous compared to after carbonization. In addition, the EDX elemental analysis revealed that the carbon content of sago bark increased from 37.5% to 97.3% following carbonization.

Gaining insights into the surface chemistry and identification of functional groups on biomass surfaces is of paramount importance as it aids in validating theories. Fourier transform infrared (FTIR) analysis is commonly employed to determine the functional groups present in a material. FTIR is widely used in characterization studies due to its speed, accuracy, and high sensitivity. Therefore, Siruru et al. (2019) characterisation study of sago bark includes an FTIR analysis of its surface chemistry. Table 2.3 summarises the FTIR analysis done by Siruru et al. (2019). The presence of a prominent peak at 1736.75 cm^{-1} signifies the presence of lignin on the surface of the material, indicating the potential of sago bark as a precursor for char production. Additionally, the detection of sulphur and phosphorus suggests that sago bark holds promise as an organic fertilizer.

Table 2.3: Various functional groups found on sago bark and their frequency ranges

Wavenumber (cm^{-1})	Functional group
1736.75	aldehydes ($\text{C}\equiv\text{C}$) and ester ($\text{C}=\text{C}$)
2350-2650	boron (B-H)
4000-3000	silicate (Si-OH)
1050-870	aromatic phosphorus (P-O)
1060-1020	sulphur (S=O)

In conclusion, the use of sago bark as a precursor of an adsorbent for the removal of wastewater contaminants is feasible, given the annual availability of sago bark waste and the high capability of sago bark to create high-quality char, as determined by characterization research conducted in the past. Hence, synthesizing magnetic activated carbon from sago bark is a sustainable environmental approach.

2.2 Optimisation by Design of Experiment (DOE)

Optimisation of process parameters can be achieved by the implementation of the design of experiment (DOE). DOE is a strategic approach to revealing the relationships between variables behind a complex system where it is based on a statistical method that deliberately manipulates input parameters while observing the associated output responses simultaneously. One of the available tools that can assist in the application of DOE is Stat-Ease Design-Expert software. Design-Expert is a software that helps in the facilitation of experimental design development with data analysis using a selected method programme within the software.

The generation of DOE from the software reveals relationships and patterns that might otherwise be complicated if using conventional approaches. Through the systematic manipulation of input parameters and observation of response variables, DOE increases the efficiency of data collection while minimising the number of experiments required. This strategy, which optimises resource allocation, is particularly advantageous when conducting experiments is expensive, time-consuming, or constrained by practical limitations. Also, an extensive array of factor combinations can be explored, all while minimising the number of trials conducted, which results in a faster completion of the analysis.

One prominent method within DOE is Response Surface Methodology (RSM), a statistical model designed to understand multivariable systems' complexity. The primary objective of RSM is to develop mathematical models and optimise responses that are influenced by several factors. This approach aims to uncover embedded interactions and provide a clearer understanding of individual variables' effects and interactions. Through RSM, the development of mathematical models that accurately represent the behaviour of

complex systems, assisting prediction, optimisation, and fine-tuning processes is made possible.

Within RSM, Box-Behnken Design (BBD) is a powerful and versatile experimental design with inherent significance to unravel complex correlations between variables and optimise complex processes. The relevance of BBD is in its capacity to effectively navigate the multidimensional space of variables, hence revealing important insights without requiring lengthy experiments. The design matrix of BBD incorporates three distinct levels for every factor: low, centre, and high. This three-level structure enables efficient analysis of the factor space, determination of quadratic relationships, and identification of potential curvature in response surfaces. In addition, including centre points in BBD improves the overall design by providing a basis to evaluate the effectiveness of fitted models and verify the resulting response surfaces.

On the other hand, using desirability functions in BBD provides valuable insights into optimal factor values. The importance levels can be given to individual responses and combined into an overall desirability score. This approach allows for evaluating combinations of factors that result in the most favourable outcomes across multiple response variables, hence assisting the development of optimal process conditions. There are several examples of previous studies done to optimise magnetic-activated carbon preparation parameters by using the RSM BBD approach, such as the preparation of magnetic-activated carbon from oil palm fibre (Marsin et al., 2020), cotton textile waste (Xu et al., 2018), and marine micro algae (Jung et al., 2019). Both preparation of oil palm fibre and marine micro algae magnetic-activated carbon optimise the impregnation ratio of metal ions to biomass, activation time, and activation temperature, while Xu et al. (2018) optimise the impregnation ratio of metals ions to activated carbon, amount of pyrrole

monomer and amount of FeCl_3 oxidant.

In conclusion, the BBD is a specific design methodology employed inside the RSM framework to assist the generation of DOE. This method's fast and analytical approach allows researchers to discover the underlying relationships, develop models of complex response surfaces, and optimise the efficiency of the processes. Also, the development of DOE and the analysis of the data can be assisted by Stat-Ease Design-Expert software. Figure 2.4 shows the process flow diagram of the process optimisation study done by using DOE.

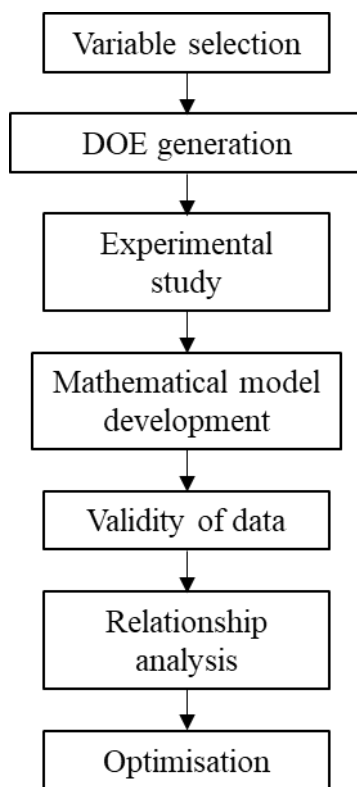


Figure 2.4: Process flow diagram of process optimisation study by using DOE

2.3 Magnetic Activated Carbon as an Adsorbent

Activated carbon is widely used on an industrial scale for the adsorption process of pollutants due to its distinctive characteristics. High porosity, a wide surface area, and strong surface reactivity make it an excellent adsorbent. The efficiency of activated carbon as an adsorbent is largely influenced by the choice of precursor and the preparation methods employed. This variability in performance can be attributed to the unique characteristics of each activated carbon, leading to a multitude of studies conducted over the past decades focused on the characterization of activated carbon. Table 2.4 shows the physical-chemical properties of activated carbon, summarized by Moosavi et al. (2020). A high adsorption capacity, which is a crucial criterion for an excellent adsorbent, is directly influenced by key properties of activated carbon such as high pore volume, BET surface area, average pore diameter, and porosity. Conversely, a high ash content is a drawback in the preparation of activated carbon as it diminishes the production yield. According to Table 2.4, activated carbon exhibits an impressive adsorption capacity, reaching levels as high as 5000 mg/g. This signifies that a single gram of activated carbon can take up to 5000 milligrams of pollutants.

Table 2.4: Physicochemical properties of activated carbon (Moosavi et al., 2020)

Adsorption capacity	5-5000 mg/g
Pore volume	0.08 – 1.5 cm ³ /g
BET surface area	500 – 3362 m ² /g
Ash content	0.2% – 37%
Average pore diameter	0.2 and 50 nm
Porosity	0.4 and 0.92

Although activated carbon is an excellent adsorbent, one of its major drawbacks is the difficulty of separating it from water bodies after the adsorption. Filtration is one of the methods to separate activated carbon from treated water. Despite that, the activated carbon

will inevitably cause filter blockage after several uses due to its microscopic size, rendering the process unsustainable and uneconomical. Given the considerable potential of activated carbon as an adsorbent, numerous studies have been conducted to address this concern. Notably, Oliveira et al. (2002) explored the utilization of magnetic particles in conjunction with activated carbon for the adsorption of pollutants from wastewater. The schematic diagram in Figure 2.5 depicts how magnetic activated carbon is recovered and reused.

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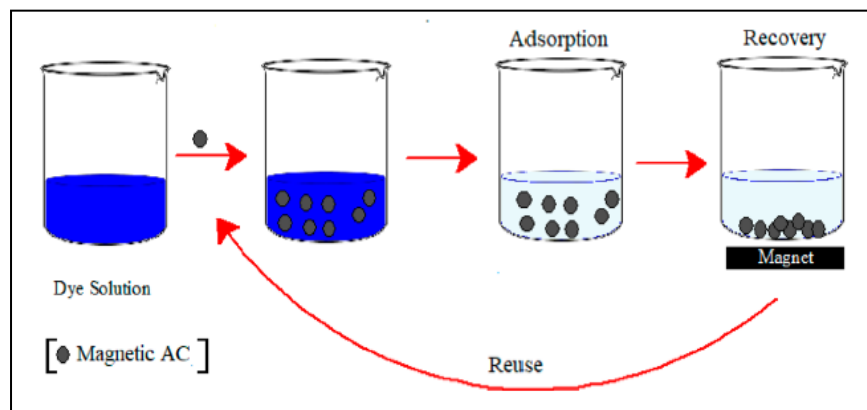


Figure 2.5: Magnetic activated carbon recovery and reuse process schematic drawing (Moosavi et al., 2020)

In past decades, there has been a significant interest in the potential of magnetic particles to solve various environmental issues. Activated carbon coated with magnetic particles makes adsorbent separation and recovery easier by supplying a magnetic field. Considering the advantageous combination of activated carbon's high adsorption capacity and the rapid magnetic separation process, the incorporation of magnetic particles into activated carbon holds the potential to significantly enhance the efficiency of the wastewater treatment industry. Table 2.5 summarizes the synthesis of magnetic activated carbon (MAC) utilizing different precursors. Table 2.5 includes a simplified MAC preparation procedure and SEM and FTIR analysis.

As demonstrated in Table 2.5, MAC's preparation methods include co-precipitation of magnetic materials into prepared activated carbon, one-step pyrolysis, which involves both magnetic particle impregnation and activation simultaneously, and two-step pyrolysis. The co-precipitation method was done to prepare MFMPAC and $\text{Fe}_3\text{O}_4\text{-AC}$ while one-step synthesis was done for $\text{CO}_2\text{-MAC}$, a-MAC, and WB(Ni)0.5. Physical method activation and chemical activation by ZnCl_2 were used to prepare activated carbon from peach stone and chestnut shell, respectively. After preparing activated carbon, peach stone, and chestnut activated carbon was co-precipitated at 70°C with $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, and FeCl_3 and $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, respectively. On the other hand, $\text{CO}_2\text{-MAC}$, a-MAC, and WB(Ni)0.5 were prepared by impregnating magnetic particles into the precursor of peanut shells, coconut shells, and wakame powder, respectively. Iron-loaded peanut shell powder was then carbonized under the CO_2 atmosphere to produce $\text{CO}_2\text{-MAC}$, while a-MAC and WB(Ni)0.5 were carbonized under the N_2 atmosphere. In contrast, MMAC production involves two stages of pyrolysis. The biomass was pyrolyzed first to produce activated carbon, then impregnated with iron oxide to produce magnetic activated carbon.

MFMPAC, Fe₃O₄-AC, CO₂-MAC, a-MAC, and MMAC used iron oxide as the magnetic material, and nickel oxide was used as magnetic particles for WB(Ni)0.5. Iron oxide is frequently used as a magnetic material because it is inexpensive, has high-quality magnetisation, and is biocompatible compared to other metal oxides (Jain et al., 2018).

On the other hand, the SEM and FTIR analysis of MAC were also compiled in Table 2.5. Based on SEM analysis of the different types of MAC, MAC that underwent the co-precipitation method has a more homogeneous structure than the MAC that was produced using the impregnation method due to the filling of magnetic materials into the pores of MAC. Thus, impregnating magnetic materials into biomass is better for producing a high porosity MAC than the co-precipitation method, as co-precipitation may block existing pores. As for the FTIR analysis of MAC from Table 2.5, vibration at a range of 500-600 cm⁻¹ was observed, which proves the presence of metal ions on the surface of MAC which can be observed from FTIR analysis of MFMPAC, a-MAC, Fe₃O₄-AC, WB(Ni)0.5, and MMAC. Aside from metal ions' functional groups, more than two functional groups on the surface of MAC can also be observed, such as hydroxyl, amine, carbonyl, and alkenes. Therefore, MAC is abundant in functional groups that will aid in the chemical adsorption of pollutants.

In conclusion, magnetic activated carbon has significant potential in the wastewater treatment industry due to its excellent properties, supported by previous research. The high efficiency of activated carbon was enhanced by incorporating it with magnetic material to facilitate regeneration. The magnetic activated carbon production process is also simple, which will benefit its application on a large scale. However, the current MAC cannot outperform the efficiency of conventional adsorbents and the current adsorption process. Therefore, an adsorption study was necessary prior to implementing MAC in the industry

to optimize its efficiency in adsorbing pollutants from wastewater. Also, based on a review of previous research on MAC, there appears to be a lack of papers on MAC synthesis utilising RSM, which will be presented in this study.

Table 2.5: Summary of different MAC with different biomass

Raw material/MAC	Reagent / Pollutant	Magnetic activated carbon preparation operating condition	Characteristics of magnetic activated carbon	References
Peanut shell/CO ₂ -MAC	FeCl ₃ ·H ₂ O / Malachite green dye	For 12 hours, FeCl ₃ ·H ₂ O was dissolved and impregnated in peanut shells. After that, the solid precursor is heated to 800°C for 90 minutes in a CO ₂ environment.	SEM micrographs showed a more cratered and fractured surface with some uniformity, which allowed dye molecules diffusion, boosted adsorbent-adsorbate contact, and increased the material's adsorption capacity. Micropores are prominent and porous features that were not seen in SEM pictures. Iron oxide nanoparticles on MAC's surface reveal well-dispersed iron particles. FT-IR spectrum of MAC shows a prominent presence of hydroxyl group, stretching vibration at 1583cm ⁻¹ (C=C), vibration at 1631cm ⁻¹ (C=O) and 1385 cm ⁻¹ (C-O), and broad band at 1104cm ⁻¹ (C-O-C).	(Feiqiang et al., 2018)
Peach stone/MFMPAC	H ₃ PO ₄ FeCl ₃ ·6H ₂ O FeCl ₂ ·4H ₂ O NaOH /	MFMPAC carbon was synthesized by physical method at	FESEM images exhibit MFMPAC nanoparticles scattered in the shape of a sphere and	(Ebadollahzadeh & Zabihi, 2020)

Table 2.5 continued

	Methylene blue dye	800°C using water vapour as a chemical agent, and then co-precipitated with 4.32 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 1.59 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and 2.56 g of NaOH for 7 minutes at 70°C.	mesoporous structures. FTIR spectra of MFMPAC show the presence of Fe-O ($568\text{--}668\text{ cm}^{-1}$), C=O and water (1633 cm^{-1}), C-NH ₂ ($1100\text{--}1150\text{ cm}^{-1}$), and C-H (2916 cm^{-1}).	
Coconut shells/a-MAC	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ / Sunset yellow food dye	Coconut shells were impregnated with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and heated to 700°C for 90 minutes in a muffle furnace with a heating rate of 20°C/min and a N_2 flow rate of 100 cm^3/min .	SEM pictures show MAC has fractures and porosity. MAC's surface likely had iron oxide nanoparticles. No peak at 3500 cm^{-1} (free hydroxyl group). FT-IR spectra show a peak for -C=O (1700 cm^{-1}), C=C (1580 cm^{-1}), C-O (1220 cm^{-1}), and Fe-O (600 cm^{-1}).	(Cazetta et al., 2016)
Chestnut shell/ Fe_3O_4 -AC	FeCl_3 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ZnCl_2 / Malachite green dye	Chestnut shells were activated with ZnCl_2 and carbonized at 700°C for 60 minutes under a 150 cm^3/min nitrogen gas flow. The FeCl_3 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were then co-precipitated with prepared AC at 70°C for 30 minutes.	The surface of Fe_3O_4 -AC seemed more homogeneous in SEM images after Fe_3O_4 filled the existing pores. FT-IR spectrum observed a stretching vibration at 2900 cm^{-1} and 1600 cm^{-1} . Small peaks were observed at 1100 to 1200 cm^{-1} , indicating the hydroxyl group and aryl alcohol, respectively. Fe-O peaks were observed at 585 cm^{-1} .	(Altintig et al., 2018)
Wakame/WB(Ni)0.5	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ KOH / Methylene blue dye	Wakame was impregnated with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ using an	SEM pictures of WB(Ni)0.5's surface show an abundance of pore structures and some dot patterns	(Yao et al., 2020)

Table 2.5 continued

		ultrasonicator. Ni-loaded wakame was combined with KOH and. pyrolyzed for 2 hours at 800°C	that appeared to be metal nickel particles. WB(Ni)0.5 FT-IR spectra reveal the presence of hydroxyl, amine, nitro compounds, and metal ions.	
Rice husk/ MMAC	ZnCl_2 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ / Methyl blue and methyl orange	Rice husk-activated carbon was impregnated with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a sonicator for 2 hours. The mixture was then pyrolyzed at 650°C for 3 hours.	SEM images show that MMAC has a porous structure and is spongy. FTIR spectra show the presence of C-H (band below 3000 cm^{-1}), -OH (around 1600 cm^{-1}), and Fe-O (590 cm^{-1}).	(Azam et al., 2020)

2.4 Dye Effluents

Dyes are essential in various industries for introducing colour to textiles, paper, plastics, leather, and more. Dyes are coloured organic compounds that can dissolve in water or oil and are designed to adhere permanently to materials (Shindhal et al., 2021). Most dyes are complex compounds with many aromatic rings that allow them to absorb particular light wavelengths and produce vivid colours (Benkhaya et al., 2020). The presence of dyes in wastewater causes a significant issue for the environment as a result of their extensive use in industries. The stable and resistant characteristics of dyes makes them difficult to degrade naturally. Consequently, when dyes enter aquatic ecosystems through industrial effluents, it can persist for extended periods, affecting water quality and aquatic life. Dyes can block sunlight penetration in water bodies, disrupting photosynthesis in aquatic plants and affecting the oxygen balance (Sasidharan et al., 2021). Additionally,

dyes can be toxic, carcinogenic, or mutagenic to aquatic organisms and humans. Effective removal of dyes from wastewater is thus crucial to mitigate their environmental impact, requiring advanced treatment methods that can efficiently adsorb and degrade these persistent pollutants.

Dyes can be categorized into various types based on their chemical structure, application methods, and source. The primary classifications include natural and synthetic dyes. Natural dyes are derived from plants, animals, or minerals, while synthetic dyes are chemically manufactured. Within these categories, several specific types are commonly used in industry as shown in Figure 2.6.

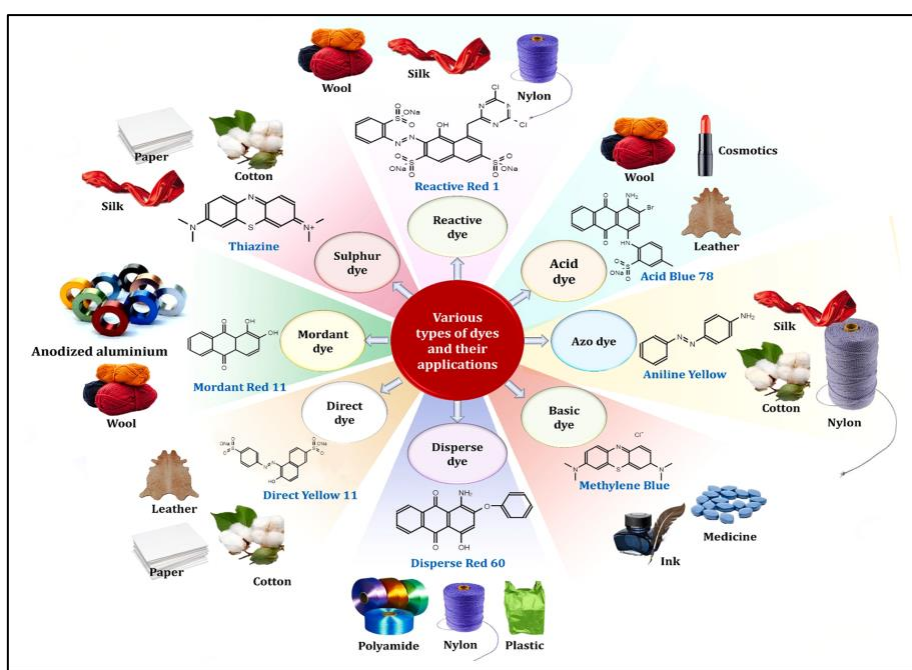


Figure 2.6: Various categories of dyes and their possible industrial applications (Al-Tohamy et al., 2020)

Reactive dyes form covalent bonds with fiber, providing excellent color fastness and versatility in application to a range of materials, including cotton and silk. Acid dyes, on the other hand, are water-soluble and primarily used for dyeing protein fibers such as wool and silk, offering vibrant colors but are not suitable for cellulosic fibers. Basic dyes,

also known as cationic dyes, are bright and mainly used for synthetic fibers like acrylics, although they have poor wash fastness. Direct dyes are soluble in water and applied to cellulosic fibers, particularly cotton, but require after-treatment for improved durability. Disperse dyes are predominantly used for synthetic fibers like polyester and necessitate high temperatures for application. Azo dyes, characterized by the presence of one or more azo groups ($-N=N-$), constitute the largest and most versatile class of synthetic dyes, offering a wide array of colors and are commonly used for dyeing both natural and synthetic fibers (Al-Tohamy et al., 2022). Mordant dyes require the use of a mordant, typically a metallic salt, to fix the dye onto the fiber, enhancing color fastness and allowing for a broader range of colors (Al-Tohamy et al., 2022; Rápó et al., 2021). Additionally, sulfur dyes are ideal for imparting dark shades on cellulosic fibers. The selection of dye type is crucial in textile coloring, as each type possesses unique characteristics and applications, ensuring the desired results are achieved.

As shown in Figure 2.6, methylene blue is classified as a basic dye or also known as cationic dye. As a cationic soluble dye, methylene blue is commonly utilised in great amount particularly in paper and textile industries as a colorant for paper and fabrics (Oladoye et al., 2022). Moreover, methylene blue also holds significant importance as a model dye in different research investigations due to its extensive use and distinctive properties. Consuming untreated or poorly treated wastewater containing methylene blue may expose individuals to health diseases such as jaundice, cyanosis, and tissue necrosis, emphasizing the importance of effective methylene blue removal from wastewater before discharge into the environment (Oladoye et al., 2022). On the other hand, given methylene blue's adaptability, investigations can be conducted to study adsorption mechanisms and

gain valuable insights into designing effective dye removal methods which serve as a significant basis for understanding the behavior of other dye contaminants.

2.5 Adsorption Process

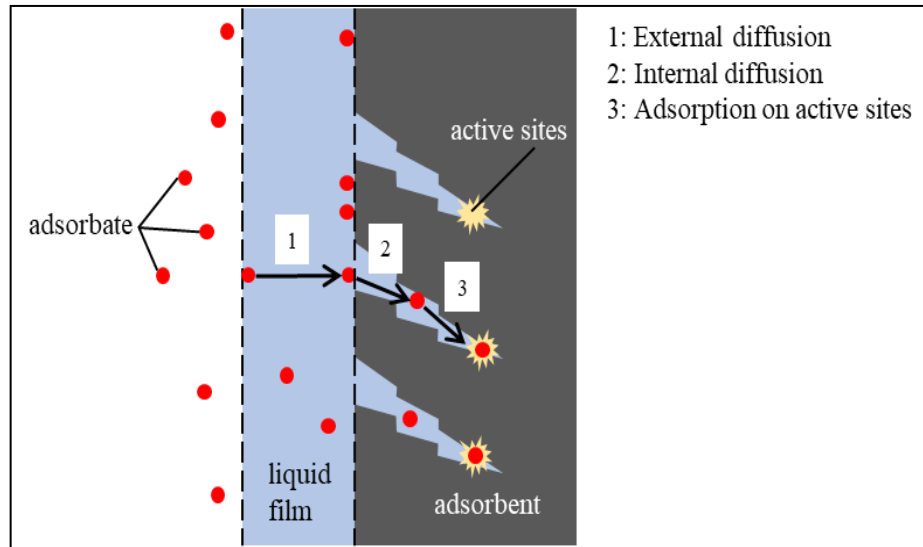


Figure 2.7: Mass transfer mechanism of adsorption

Adsorption is a surface phenomenon involving a mass transfer of two phases of substances identified as adsorbate and adsorbent. Adsorbate will accumulate on the surface of the adsorbent via physisorption, chemisorption, or physicochemical adsorption (Saleh, 2022). The process diagram of the mass transfer of adsorbate onto adsorbent is shown in Figure 2.7. The process of adsorption involves three mass transfer steps: external diffusion, internal diffusion, and adsorption onto active sites. External diffusion occurs when the adsorbate migrates from a liquid film to the pores of the adsorbent. Internal diffusion, on the other hand, takes place as the adsorbate moves within the pores of the adsorbent towards the active sites. The final step involves the successful adsorption of the adsorbate onto the surface of the adsorbent's active sites. Figure 2.7 illustrates the mass transfer mechanism of adsorption.

In wastewater treatment, adsorption is a physical method of treatment along with membrane filtration and coagulation/flocculation methods. The physical method in wastewater treatment applies the mass transfer principle to remove pollutants from the wastewater. Adsorption is highly regarded for its adaptability, simple design, potential for adsorbent reuse, cost-effectiveness, and eco-friendliness in comparison to other physical wastewater treatment methods. These advantages have garnered significant attention from researchers. Currently, the adsorption process has gained widespread acceptance as an effective method for the removal of contaminants from wastewater. The cost and applicability of adsorption for pollutant removal are greatly influenced by the type of adsorbent used, its adsorption capacity, and the reusability of the adsorbent in effectively adsorbing harmful contaminants from wastewater. The price of adsorbents will inevitably increase the cost of adsorption and the other way around. Examples of adsorbents with high adsorption uptake capacities are bio sorbents, activated carbon, biochar, clays and minerals, polymers, nanoparticles, and composites.

Adsorbents have different physicochemical properties, resulting in different adsorption behaviours and mechanisms. Due to the unique characteristics of adsorbent, scientific experiments need to be conducted to study the adsorption behaviours and mechanism of the synthesis adsorbent which include the study of the effects of pH, adsorbent dosage, contact time, temperature, and adsorbate initial concentrations. Furthermore, the adsorption mechanism of the adsorbent can also be determined by linear regression of the adsorption kinetic model and isotherm model which will evaluate the rate of adsorption and the relationship of equilibrium between adsorbent and adsorbate respectively.

2.5.1 Adsorption Kinetic Model

The study of adsorption kinetic models is a critical step in the design of adsorption systems, as it provides valuable information about the adsorption rate, performance of the chosen adsorbent, and the underlying mass transfer processes involved (Wang & Guo, 2020). Also, the adsorption kinetic model assessed the rate of reaction by determining the relationship between reactant concentration and contact time. Multiple kinetic models have been suggested, each considering the reactant concentration and the adsorption rate, comprises of pseudo-first-order (PFO), pseudo-second-order (PSO), and intra-particle diffusions.

The pseudo-first-order (PFO) kinetics model, initially proposed by Lagergren in 1898, is widely used to estimate the adsorption capacity in liquid-solid systems. High initial adsorbate concentrations are required for utilizing PFO kinetic model, and it is assumed that adsorption is not controlled by adsorption in active sites. The equation model of PFO is shown in Equation 2.1.

$$q_t = q_e (1 - e^{-k_1 t}) \quad \text{Equation 2.1}$$

Where q_e is the adsorption capacity of adsorbent at equilibrium (mg/g), q_t is the adsorption capacity at time (mg/g), k_1 is PFO rate constant (1/min) and t is the adsorption time (min). PFO parameters can be determined by plotting the graph of q_t vs. t in OriginPro software and analysing the plot using the nonlinear fitting of BoxLucas1. According to Wang and Guo (2020), the rate of adsorption is considered slow when the value of k_1 is low and the value of $(q_e - q_t)$ is higher.

Apart from PFO, pseudo-second-order (PSO) is another commonly applied kinetic model to identify the rate of adsorption. Both PFO and PSO are simplified Langmuir kinetics that were dependent on the initial concentration of adsorbate. Contrary to PFO,

The Langmuir kinetic model can be simplified as the pseudo-second-order (PSO) kinetic model only under the condition of low initial concentration of the adsorbate. Moreover, the high correlation of the PSO kinetic model suggests a strong association with the presence of abundant active sites on the surface of the adsorbent (Wang & Guo, 2020). Thus, any adsorption that follows PSO kinetic models can be assumed to be rich in active sites. To determine PSO parameters PSO equation model was linearised as described in the following equation:

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

$$h = k_2 q_e^2 \quad \text{Equation 2.3}$$

Where k_2 is the PSO rate constant (g/mg·min) and h is the initial sorption rate ((mg/g)/min). PSO parameter can be determined by plotting a linear graph of t/q_t vs t . The slope and y-intercept of the graph will determine the equilibrium adsorption capacity and rate constant of the process.

Intra-particle diffusion (ID) model is another commonly used kinetic model to determine the mass transfer mechanism involved during the adsorption of adsorbate onto the adsorbent. Unlike the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models, the internal diffusion (ID) model assumes that the diffusion of the adsorbate into the pores of the adsorbent is the slowest step in the adsorption mass transfer process, while the diffusion of the adsorbate onto the active sites occurs more rapidly. The Weber and Morris model is commonly employed to describe the internal diffusion of the adsorbate during adsorption and determine the rate-limiting step, thanks to its simplicity and ease of use. Equation 2.4 shows the linear equation of the Weber and Morris ID kinetics

model.

$$q_t = k_{id} t^{1/2} + c \quad \text{Equation 2.4}$$

Where, k_{id} is the rate constant of ID ($\text{mg/g.min}^{1/2}$), $t^{1/2}$ is the half-life times (s), and c is the boundary thickness of the liquid film (mg/g). ID model can be determined by plotting the graph of q_t vs $t^{1/2}$. From the graph, it can be expected that the adsorption is controlled by intra-particle diffusion if the intercept of the linear graph is found at (0,0) else, the adsorption is controlled by multiple processes (Wang & Guo, 2020).

Table 2.6: Summary of adsorption kinetic models

Adsorption kinetic model	Equation	Assumptions
Pseudo-first order (PFO)	$q_t = q_e (1 - e^{-k_1 t})$	- adsorption is not controlled by adsorption in active sites. - the rate of adsorption is considered slow when the value of k_1 is low and the value of $(q_e - q_t)$ is higher.
Pseudo-second order (PSO)	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	strong association with the presence of abundant active sites on the surface of the adsorbent
Intra-particle diffusion (ID)	$q_t = k_{id} t^{1/2} + c$	- the diffusion of the adsorbate into the pores of the adsorbent is the slowest step in the adsorption mass transfer process, while the diffusion of the adsorbate onto the active sites occurs more rapidly. - adsorption is controlled by intra-particle diffusion if the intercept of the linear graph is found at (0,0) else, the adsorption is controlled by multiple processes.

2.5.2 Adsorption Isotherm Model

Adsorption isotherms play a vital role in assessing the adsorption capacities of adsorbent materials and establishing the equilibrium relationship between adsorbent and adsorbate at a constant temperature. A proper understanding and interpretation of adsorption isotherms are crucial for comprehending the adsorption mechanism pathways and facilitating the successful design of adsorption systems (Ayawei et al., 2017). Langmuir, Freundlich, Temkin, and Dubinin-Raduskevich (DR) models are the common isotherm models utilized to characterise the adsorption mechanism of adsorbent. All the equation models will be using linear regression analysis to further characterize the adsorption mechanism and due to the bias caused by linearization, many error functions were implemented to compensate for it. The linear regression analysis has gained significant popularity as a method for determining accurate adsorption isotherm models due to its capability to quantify the distribution of adsorbates, evaluate the adsorption system, and validate the theoretical assumptions underlying the models (Ayawei et al., 2017).

2.5.2.1 Langmuir isotherm model

The Langmuir isotherm model is one of the popular isotherm models introduced in the year 1918 where it defined the maximum monolayer adsorption capacity of the adsorbent using the linearized Langmuir isotherm model shown as Equation 3.1.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}}C_e \quad \text{Equation 2.5}$$

Where C_e and q_e are the concentration of adsorbate and adsorption capacity of adsorbate at equilibrium respectively, q_{max} is the maximum monolayer adsorption capacity of adsorbent (mg/g) and K_L is Langmuir isotherm model constant (L/mg). The isotherm model constant

can be solved by plotting the linear graph of C_e/q_e vs C_e . Another characteristic that can be determined by the Langmuir isotherm model is the separation factor, R_L . R_L is a unitless constant that can be described by Equation 3.2.

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{Equation 2.6}$$

Where C_0 is the initial concentration of adsorbate. The calculated value of K_L from linear regression of Langmuir isotherm model is used to determine the R_L value. The acquired value of R_L will be analysed by the following indications:

$R_L > 1$: adsorption is unfavourable

$0 < R_L < 1$: adsorption is favourable

$R_L = 1$: adsorption is linear

$R_L = 0$: adsorption is irreversible

The disadvantage of Langmuir isotherm is it signifies only the monolayer adsorption of adsorbate onto the surface of the adsorbent which is frequently unable to reflect the experimental isotherm data described for aqueous solution adsorption particularly, activated carbon (Worch, 2021). Langmuir isotherm model states two assumptions; adsorption of adsorbate only occurs once on the adsorption sites, reflecting there is only monolayer adsorption occurs and single adsorption site only binds with one single adsorbate due to energetic homogeneity of the adsorption sites (Singh et al., 2021). Yet, Langmuir's isotherm model equation was found to be useful in situations where the basic assumptions were blatantly violated.

2.5.2.2 Freundlich isotherm model

The Freundlich isotherm model is applicable to adsorption processes occurring on heterogeneous surfaces. Moreover, it offers an expression for surface heterogeneity, incorporating the exponential distribution of active sites and their corresponding energies

(Ayawei et al., 2017). Freundlich isotherm describes a moderate concentration well and commonly use to describe activated carbon adsorption in an aqueous solution (Worch, 2021). The linear form of Freundlich isotherm model can be expressed as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{Equation 2.7}$$

Where K_f and $1/n$ are the Freundlich isotherm parameters. K_f is the adsorption coefficient that characterizes the intensity of adsorption $((\text{mg/g}) \cdot (\text{mg/L})^{1/n})$. A higher value of K_f indicates a higher loading of adsorbent onto adsorbent can be reached. Meanwhile, $1/n$ is correlated to the energetic heterogeneity of the adsorbent surface and favourably of the adsorbent loading. The values of $1/n$ can be described by the following relation:

$1/n = 1$: isotherm model is linear

$1/n < 1$: favourable isotherm as it displays a high adsorbent loading at low concentrations

$1/n > 1$: unfavourable

Values of K_f and $1/n$ can be determined by the linear plot of $\log q_e$ and $\log C_e$.

2.5.2.3 Temkin isotherm model

It is assumed in the Temkin isotherm model that the heat of adsorption (ΔH_{ads}) of all molecules in the layer reduces linearly with increase surface coverage, and that indirect adsorbate-adsorbent relations do not effect on the adsorption process (Ayawei et al., 2017). Constant distribution of the bonding energy also can be defined using the Temkin isotherm model (Wadhawan et al., 2020). In practice, Temkin isotherm is only applicable to moderate concentrations of adsorption. Following equations are used to describe the linear form of the Temkin isotherm model:

$$q_e = \frac{RT}{b} \ln A_T + \frac{RT}{b} \ln C_e \quad \text{Equation 2.8}$$

$$B = \frac{RT}{b} \quad \text{Equation 2.9}$$

$$q_e = B \ln A_T + B \ln C_e \quad \text{Equation 2.10}$$

where R is the universal gas constant (8.314 J/mol.K), T is the adsorption temperature (K), b is the Temkin isotherm constant, A_T is the Temkin isotherm equilibrium binding constant (L/g) and B is Temkin constant related to the heat of adsorption (J/mol). Values of the Temkin constant can be determined by the plot of q_e vs $\ln C_e$ linear graph by calculating the gradient and the y-intercept of the linear graph.

2.5.2.4 Dubinin-Radushkevich (DR) isotherm model

Dubinin-Radushkevich (DR) isotherm model is originally developed for vapour adsorption onto microporous adsorbent in 1947 based on the theory of pores filling mechanism (Worch, 2021). The Freundlich isotherm model is frequently employed as an empirical adsorption model to describe adsorption mechanisms on heterogeneous surfaces, assuming a Gaussian energy distribution. However, it exhibits unrealistic asymptotic behaviour and lacks the ability to accurately predict Henry's law at low pressures. As a result, this isotherm is best suited for moderate ranges of adsorbate concentrations.

The model considers multilayer adsorption with the involvement of Van der Waals forces and is primarily applicable to physical adsorption processes. It serves as a fundamental equation for qualitatively characterizing the adsorption of gases and vapours on microporous sorbents. Since the DR isotherm model does not consider a homogeneous surface and constant adsorption potential, it is seen as being preferable to the Langmuir isotherm model (Hu & Zhang, 2019). Moreover, it can also be used to describe the aqueous solution adsorption by a modified form for solutes as shown in Equation 2.11.

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad \text{Equation 2.11}$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad \text{Equation 2.12}$$

$$E = \frac{1}{\sqrt{2\beta}} \quad \text{Equation 2.13}$$

Where q_m is the maximum adsorption capacity of the adsorbent (mg/g), β is the DR constant related to adsorption energy, ε is Polanyi potential and E is mean free energy (kJ/mol). The value of β can be used to estimate mean free energy based on Equation 2.13 which is employed for differentiating the adsorption processes (Hu & Zhang, 2019). The adsorption is considered physical adsorption when E is less than 8 kJ/mol while it went through chemical adsorption when E is greater than 16 kJ/mol. Also, when E is in the range of 8-16 kJ/mol, the adsorption process is dominated by ion exchange (Dinh et al., 2019).

Table 2.7: Adsorption isotherm parameters of different adsorbents for methylene blue removal

Adsorbent	Adsorption isotherm parameters		Ref.
Magnesium silica-coated magnetized palm shell-activated carbon	<u>Langmuir</u> $K_L = 0.02563 \text{ mg/g}$ $q_{max} = 369.54 \text{ mg/g}$ $R^2 = \mathbf{0.995}$		(Kittappa et al., 2020)
Magnetic wakame biochar nanocomposites	<u>Langmuir</u> $K_L = 3.549 \text{ mg/g}$ $q_{max} = 552.48 \text{ mg/g}$ $R^2 = \mathbf{0.998}$	<u>Freundlich</u> $K_F = 407.07 \text{ (mg/g)} \cdot (\text{L/mg})^{1/n}$ $1/n = 0.1478$ $R^2 = 0.993$	(Yao et al., 2020)
Magnetic ball-milled activated carbon (hickory chip)	<u>Langmuir</u> $K_L = 63.616 \text{ mg/g}$ $q_{max} = 304.2 \text{ mg/g}$ $R^2 = \mathbf{0.973}$	<u>Freundlich</u> $K_F = 201.744 \text{ (mg/g)} \cdot (\text{L/mg})^{1/n}$ $1/n = 0.097$ $R^2 = 0.871$	(Li et al., 2020)
Nano-magnetic activated carbon (peach stone and wood)	<u>Langmuir</u> $K_L = 0.376 \text{ mg/g}$ $q_{max} = 434.128 \text{ mg/g}$ $R^2 = 0.9455$	<u>Freundlich</u> $K_F = 159.748 \text{ (mg/g)} \cdot (\text{L/mg})^{1/n}$ $1/n = 0.297$ $R^2 = \mathbf{0.991}$	(Ebadollahzadeh & Zabihi, 2020)

Table 2.7 continued

Magnetic alginate/rice husk bio-composite beads	<u>Langmuir</u> $K_L = 4.43 \text{ mg/g}$ $q_{max} = 344.0 \text{ mg/g}$ $R^2 = 0.994$ <u>Dubinin-Radushkevich</u> $q = 315.92 \text{ mg/g}$ $E = 5.0 \text{ kJ/mol}$ $R^2 = 0.984$	<u>Freundlich</u> $K_F = 7.41(\text{mg/g}) \cdot (\text{L}/\text{mg})^{1/n}$ $1/n = 0.607$ $R^2 = 0.999$	(Alver et al., 2020)
Magnetic-activated carbon-cobalt nanoparticles (sea-buckthorn stone)	<u>Langmuir</u> $K_L = 0.1171 \text{ mg/g}$ $q_{max} = 192.3 \text{ mg/g}$ $R^2 = 0.9996$ <u>Temkin</u> $A_T = 2.923 \text{ L/mol}$ $B = 34.755$ $R^2 = 0.9717$	<u>Freundlich</u> $K_F = 65.34 (\text{mg/g}) \cdot (\text{L}/\text{mg})^{1/n}$ $1/n = 0.2345$ $R^2 = 0.9449$	(Mohammadi et al., 2020)
Magnetic mesoporous carbon adsorbent (rice husk)	<u>Langmuir</u> $K_L = 0.0148 \text{ L/mg}$ $R^2 = 0.4264$	<u>Freundlich</u> $K_F = 0.769 (\text{mg/g}) \cdot (\text{L}/\text{mg})^{1/n}$ $1/n = 1.3091$ $R^2 = 0.9543$	(Azam et al., 2020)
Eucalyptus sawdust magnetic activated carbon	<u>Langmuir</u> $K_L = 99.48 \text{ mg/g}$ $q_{max} = 192.31 \text{ mg/g}$ $R^2 = 0.9912$ <u>Dubinin-Radushkevich</u> $q_m = 193.87 \text{ mg/g}$ $E = 46.65 \text{ kJ/mol}$ $R^2 = 0.8971$	<u>Freundlich</u> $K_F = 90.28 (\text{mg/g}) \cdot (\text{L}/\text{mg})^{1/n}$ $1/n = 0.126$ $R^2 = 0.9702$ <u>Temkin</u> $A_T = 171.96 \text{ L/mol}$ $B = 158.66$ $R^2 = 0.9283$	(Chen et al., 2019)
Magnetic ZnCl_2 -activated carbon (coconut shell)	<u>Langmuir</u> $K_L = 0.047 \text{ mg/g}$ $q_{max} = 156.25 \text{ mg/g}$ $R^2 = 0.9157$	<u>Freundlich</u> $K_F = 20.99 (\text{mg/g}) \cdot (\text{L}/\text{mg})^{1/n}$ $1/n = 0.3436$ $R^2 = 0.9506$	(Yağmur & Kaya, 2021)

Table 2.8: Summary of adsorption isotherm model

Adsorption isotherm model	Equation	Mechanisms
Langmuir isotherm model	$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{1}{q_{max}} C_e$	• adsorption of adsorbate only occurs once on the adsorption sites, reflecting there is only monolayer adsorption occurs. • single adsorption site only binds with one single adsorbate due to energetic homogeneity of the adsorption sites.
Freundlich isotherm model	$\log q_e = \log K_f + \frac{1}{n} \log C_e$	• adsorption processes occurring on heterogeneous surfaces.
Temkin isotherm model	$q_e = \frac{RT}{b} \ln A_T + \frac{RT}{b} \ln C_e$	• the heat of adsorption (ΔH_{ads}) of all molecules in the layer reduces linearly with increase surface coverage, and that indirect adsorbate-adsorbent relations do not effect on the adsorption process
Dubinin-Raduskevich (DR) isotherm model	$\ln q_e = \ln q_m - \beta \varepsilon^2$	• considers multilayer adsorption with the involvement of Van der Waals forces and is primarily applicable to physical adsorption processes.

2.5.3 Effect of Temperature

The temperature of the solution during the adsorption process is also one of the adsorption parameters that could affect the efficiency of the adsorbent during the process. Normally, a higher adsorption temperature will increase the adsorption efficiency as at high temperature the viscosity of the solution will decrease which causes a faster diffusion of adsorbate molecules into the surface of adsorbent active sites. The impact of temperature on the adsorption process can determine whether it is thermodynamically

exothermic or endothermic. In an exothermic adsorption process, the adsorption capacity decreases as the temperature rises, while in an endothermic process, the adsorption capacity increases with decreasing temperature. By conducting adsorption experiments at varied temperatures, thermodynamic parameters of adsorbent can be obtained which will help to predict the feasibility and spontaneity of the process.

The feasibility of the adsorption process at controlled temperatures can be decided by determining the standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0). These thermodynamic parameters of the process can be solved by considering a few assumptions; the adsorption layer is assumed to be a distinct phase from the bulk phase and the adsorbents are thermodynamically inert. By considering the assumption, more distinct ways of thermodynamics concept can be applied to adsorption equilibrium. All the parameters can be determined by Van't Hoff reaction isotherm equations which is the relationship between free energy change (ΔG), standard free energy change (ΔG^0) and equilibrium constant (K) at a constant temperature (T) which is shown in Equation 2.14. Equation 2.15 is the reduced Van't Hoff equation under the assumption of free energy is equal to zero when the adsorption already achieved equilibrium.

$$\Delta G = \Delta G^0 + RT \ln K \quad \text{Equation 2.14}$$

$$\Delta G^0 = -RT \ln K \quad \text{Equation 2.15}$$

Where R is the ideal gas constant at $8.314 \text{ J mol}^{-1}\text{K}^{-1}$. Meanwhile, ΔH^0 and ΔS^0 can be determined by linear regression of $\ln K$ versus $1/T$ plot by inserting Equation 2.16 into Equation 2.15. Equation 2.16 is the equation that relates all three thermodynamic parameters. Equation 2.17 is the linearized Equation 2.16 to determine the values of ΔH^0

and ΔS^0 . The values of ΔH^0 and ΔS^0 can be determined from the obtained slope and y-intercept of the linear regression respectively.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{Equation 2.16}$$

$$\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \text{Equation 2.17}$$

The feasibility of adsorption thermodynamics can be predicted from the calculated ΔG^0 while the weight and the significance of ΔG^0 depend on ΔH^0 and ΔS^0 values. According to Doke and Khan (2013), adsorption is always feasible and spontaneous when the value of ΔG^0 is less than zero and when the value ΔG^0 is more than zero, the adsorption process is considered as non-feasible and non-spontaneous. Meanwhile, the heat reaction of the adsorption process can be predicted by the sign of ΔH^0 value. Negative values of ΔH^0 will indicate that the adsorption process is exothermic and positive values of ΔH^0 indicate that the adsorption process is an endothermic process. The spontaneity of the process can be predicted by taking note of all thermodynamic parameters of the adsorption. After determining the feasibility and the heat reaction that took place during the process using ΔG^0 and ΔH^0 respectively, the sign of ΔS^0 will determine the spontaneity of the process. If the process is exothermic and ΔS^0 is a positive value, adsorption happens spontaneously at all temperatures whereas, the adsorption is only spontaneous when $\Delta H^0 > T\Delta S^0$ when ΔS^0 has a negative value. On the other hand, if the process is an endothermic process with a positive ΔS^0 value, the process is considered a spontaneous process at $\Delta H^0 > T\Delta S^0$ and spontaneous at no temperature when ΔS^0 has a negative value.

Insights on the role of temperature throughout the adsorption will help in optimizing the usage of adsorbent in adsorbing the pollutants from the water system. The adsorption of pollutants onto the surface of adsorbents can be either spontaneous or not.

The spontaneity of the process will ease the adsorption process which is the real objective of temperature study because adsorption will occur at any temperature which will lower the cost of adsorption on temperature control. Table 2.9 shows the thermodynamic parameters of different magnetic adsorbents performed with methylene blue. From Table 2.9, it is shown that each of adsorbent react differently during the adsorption process at different temperatures which made the study of the effect of temperature necessary to characterize adsorbent behaviours towards adsorbent during the process.

Table 2.9: Thermodynamic parameters of different adsorbents for methylene blue adsorption

Adsorbent	T (K)	ΔG^0 (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)	Ref.
Magnetic graphene-carbon nanotube composite	283	-4.6529	8.7201	47.22	(Wang et al., 2014)
	293	-5.0719			
	303	-5.5917			
	313	-6.0547			
Mesoporous magnetic silica composite	298	-2.541	-5.370	-9.340	(Ye et al., 2020)
	308	-2.527			
	318	-2.474			
	328	-2.238			
Modified montmorillonite	278	-3.46	24.483	102.33	(Rahmani et al., 2020)
	303	-7.45			
	323	-8.61			
	353	-11.22			
Carboxymethyl cellulose-coated Fe ₃ O ₄ -SiO ₂ core-shell magnetic nanoparticles	298	-2.64	22.73	82.5	(Zirak et al., 2018)
	303	-3.09			
	313	-3.97			
	323	-4.74			
Magnetic-activated biochar nanocomposites derived from wakame	293	-29.86	49.57	269.87	(Yao et al., 2020)
	303	-31.67			
	313	-35.06			
	323	-37.86			
Magnetic ZnCl ₂ activated carbon from coconut shell	298	-4.42	18.57	77.0	(Yağmur & Kaya, 2021)
	308	-5.10			
	318	-5.96			

2.5.4 Effect of Adsorbent Dosage

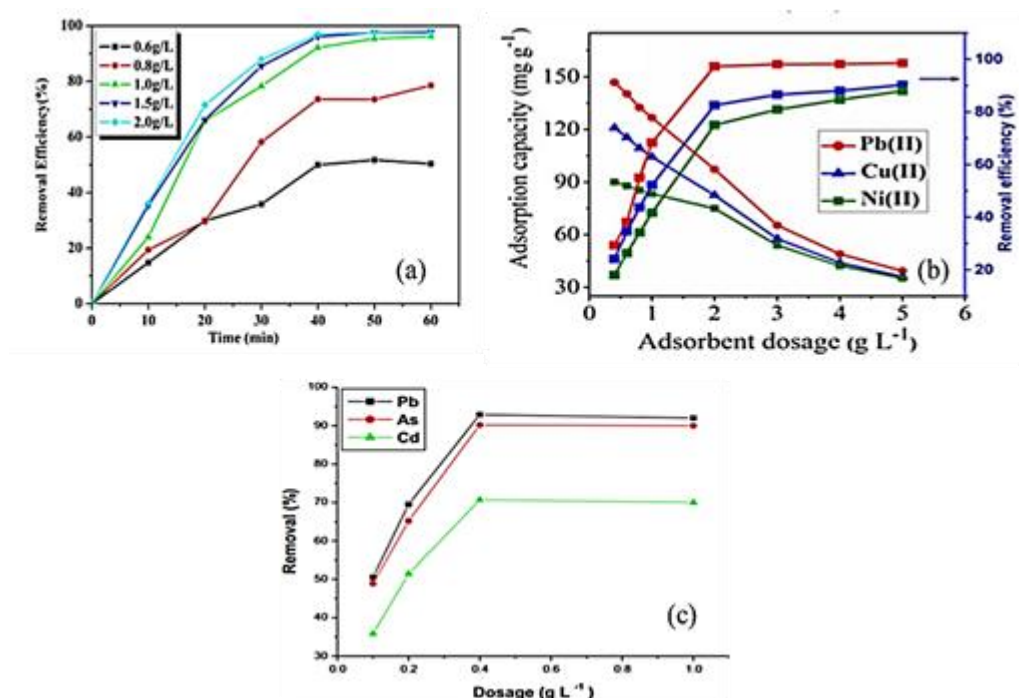


Figure 2.8: Effect of dosage of (a) magnetic activated semi-coke on rhodamine dye (Gao et al., 2016), (b) MACCC on Pb(II), Cu(II) and Ni(II) (Le et al., 2019), and (c) Fe₃O₄NP@AC@C₄H₈SO₃H on Pb(II), As(III) and Cd(II) ions removal (Nejadshafiee & Islami, 2019)

The effect of adsorbent dosage is a study to determine how to optimize the amount of adsorbent use to adsorb the unwanted pollutants. Different dosages of adsorbent will be introduced to the aqueous solution that contains the same concentration of pollutants. From there, the percentage of removal of pollutants will be calculated to determine the most optimum dose of adsorbent needed to remove the pollutants. The dosage of adsorbent plays a significant role in the adsorption process as it directly affects the cost by minimizing the quantity of adsorbent used. Typically, an increase in adsorbent dosage leads to a higher percentage of removal of pollutants due to the greater number of active sites available on the adsorbent surface. However, there is a limit beyond which introducing an excessive amount of adsorbent may result in agglomeration, leading to a decrease in pollutant

removal efficiency. Agglomeration of adsorbent will decrease the number of active sites due to the lesser surface area leading to lower adsorption capacity. Thus, studying the influence of adsorbent dosage on the adsorption of pollutants will assist in determining the most optimum amount of adsorbent needed per volume of pollutants which later become beneficial from an economic standpoint.

From the research studies reported by Gao et al. (2016), Le et al. (2019), and Nejadshafiee and Islami (2019), Figure 2.8 shows the effect of adsorbent dosage on removal efficiency of three different adsorbent towards different types of adsorbates. Figure 2.8(a) shows a study done by Gao et al. (2016) to remove rhodamine dye using magnetic-activated semi-coke at 5 different adsorbent dosages ranging from 0.6 g/L to 2 g/L. The removal efficiency of rhodamine dye was collected every 10 minutes for 60 minutes. From the graph plotted, a 100% removal percentage was achieved at adsorbent dosage of more than 1.0 g/L within 60 minutes of adsorption time. Thus, 1.0 g/L is selected as the most optimum adsorbent dosage for the adsorption of rhodamine dye by using magnetic-activated semi-coke. On the other hand, Figure 2.8(b) shows the study of adsorbent dosage done by Le et al. (2019) on the adsorption of Pb(II), Cu(II), and Ni(II) by using a composite of magnetite, activated carbon from spent coffee grounds and natural clay (MACCC) at a dosage range of 0.4 g/L to 5 g/L. From the data plotted, the increase in MACCC dosage to the system increased the removal efficiency of the heavy metal ions and decreased the adsorption capacity of the adsorbents simultaneously. However, adsorption of Pb(II), Cu(II), and Ni(II) almost reach saturation value at MACCC dosage of 2 g/L where only a small increase of removal efficiency occurs when the dosage increases to 3 g/L and higher. Reduced adsorption capability may be caused by overlapping or aggregation of adsorption sites. Thus, 2 g/L is selected as the optimum dosage for Pb(II),

Cu(II), and Ni(II) removal using MACCC as it is the minimum dosage of MACCC to achieve the highest removal efficiency. Meanwhile, Figure 2.8(c) shows the study done for the adsorption of Pb(II), As(III) and Cd(II) ions by sulfone-modified magnetic activated carbon ($\text{Fe}_3\text{O}_4\text{NP}@AC@C_4H_8\text{SO}_3\text{H}$). The effect of $\text{Fe}_3\text{O}_4\text{NP}@AC@C_4H_8\text{SO}_3\text{H}$ dosage was studied at a range of 0.1 g/L to 1.0 g/L. An adsorbent dosage of 0.4 g/L was chosen as the most optimum dosage in adsorbing Pb(II), As(III) and Cd(II) as the removal efficiency stop increasing even after increasing the adsorbent dosage from 0.4 g/L. From all three examples of the study of the effect of adsorbent to adsorption, it was concluded that increasing the adsorbent dosage will increase the removal efficiency of pollutants from the system. However, the removal efficiency will not increase when the saturation values are already achieved.

2.5.5 Effect of pH

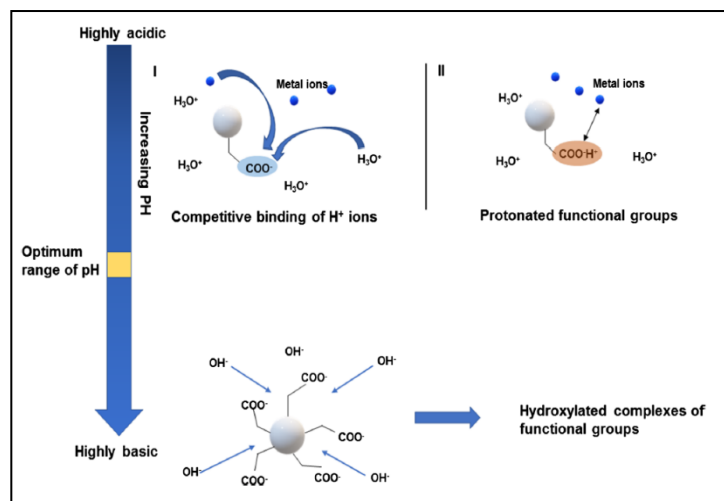


Figure 2.9: Effect of pH on the adsorption (Singh et al., 2021)

The study of pH effects on the adsorption process is crucial to knowing that pH has a significant impact on ion exchange and electrostatic interactions that occur during the adsorption. Generally, it is known that a pH level of 1 to 6 is known as acidic while a pH level of 8 to 12 is basic. Also, the acidity and alkalinity of the solution are based on the

concentration of H^+ and OH^- ions present in the solution respectively. The lower the pH, the higher the concentration of H^+ and vice versa. Figure 2.9 shows the effect of pH on the adsorption process.

The low adsorption capacity of adsorbent at lower pH is generally caused by the competitiveness of positively charged dye ions to adsorb on the surface adsorbent with H_3O^+ ions and due to the high amount of proton that protonate with negatively charged adsorbent. On the other hand, the low adsorption capacity at high pH value is due to high concentrations of hydroxylated complexes which destroyed the surface causing the decreased of adsorbent active sites. Thus, optimizing the adsorbent's performance requires maintaining a moderate pH range during the adsorption process (Singh et al., 2021).

The study of pH during the adsorption process is to determine the adsorbent point of zero charge pH (pH_{PZC}). pH_{PZC} is one of the significant adsorbent characteristics at which the zeta potential of adsorbents is equal to zero which explains to no electrostatic interactions will occur at pH_{PZC} . When the pH is less than the pH_{PZC} value, more H^+ can be exchanged for cations pollutants and the high concentration of H^+ will protonate the surface functional group of adsorbents increasing the amount of surface positive charges (Duan et al., 2020). Due to electrostatic repulsion, the adsorption of cation pollutants would then be impeded, whereas the adsorption of anions would improve. On the other hand, when the pH is raised to levels above pH_{PZC} , deprotonation restores the negative charge to the adsorbent's functional group, demonstrating the opposing impact of cations and anions (Wadhawan et al., 2020).

In conclusion, in a high pH adsorbate condition, the pH_{PZC} of adsorbent should be more acidic, and alkaline at low pH conditions. However, the adsorption capacity of

pollutants is also affected by their ionic form and each pollutant's ionic forms have a different attraction to functional groups.

2.5.6 Effect of Initial Concentration of Adsorbate

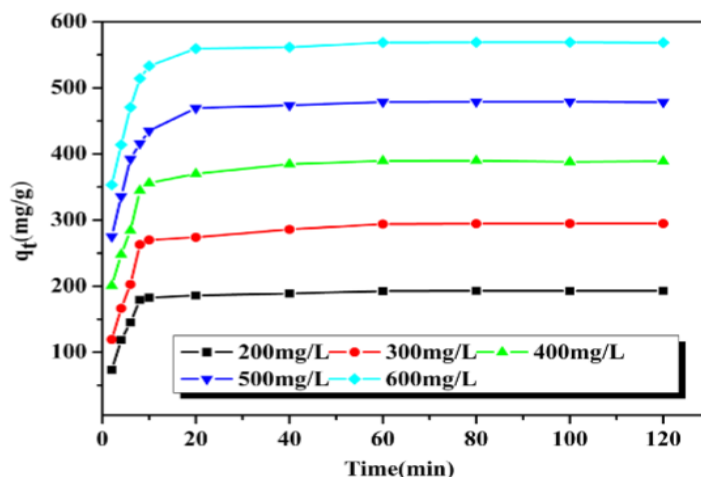


Figure 2.10: Effect of initial concentration of Rhodamine dye on adsorption capacity (Gao et al., 2016)

The common objective of the study of the effect of initial concentrations of adsorbate is to determine at maximum capacity uptake of the adsorbent. At low concentrations, the accessibility of dye ions for adsorption is limited, resulting in decreased adsorption efficiency. As the concentration increases, a greater number of ions become available for adsorption, leading to an enhanced adsorption rate. However, after a specific concentration is reached, the number of saturated sites can no longer adsorb any more ions. Therefore, the adsorption effectiveness falls for the same quantity of adsorbent which makes the fall in the adsorption rate. Based on the study by Gao et al. (2016), the adsorption rate of rhodamine dye for the first 10 minutes is high compared to the rate after 10 minutes of adsorption. According to Gao et al. (2016), the adsorption of Rhodamine dye initially takes place on the exterior surface of the adsorbent within the first 10 minutes. However, after this period, the adsorbent's exterior surface becomes saturated, leading to

the occurrence of internal diffusion of Rhodamine dye into the pore structure of the adsorbent. This internal diffusion process results in a slower adsorption rate. The graph of different initial concentrations of rhodamine dye adsorption capacity vs adsorption time is shown in Figure 2.10.

2.6 Summary

In summary, while activated carbon is widely recognised for its effectiveness in dye removal, the specific use of sago bark as a biomass for synthesising magnetically activated carbon is significantly underexplored. Previous studies have highlighted the potential of various biomass-derived magnetically activated carbons, but the optimisation of sago bark-derived MAC using Design-Expert software and the Box-Behnken design remains insufficiently investigated. Furthermore, comprehensive characterisation using techniques like BET, SEM-EDX, and FTIR, as well as the evaluation of adsorption behaviours under diverse conditions, have not been fully addressed for sago bark-derived magnetically activated carbon. This research aims to fill these gaps by focusing on the synthesis and optimization of sago bark magnetic-activated carbon (SBMAC), thoroughly characterizing its properties, and assessing its efficiency in removing methylene blue dye under various conditions. Through this study, we aim to provide valuable insights and advancements in the field of environmental remediation, employing the distinct properties of sago bark as a novel biomass source.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

Figure 3.1 shows the process flowchart of research methodology based on the three objectives of the research. Optimum process parameters were determined by preparing SBMAC from the generated DOE using Design-Expert software. The most optimal process parameters were used to synthesise SBMAC, and methylene blue solution was prepared for use in adsorption experiments to evaluate kinetics, isotherms, temperature effects, adsorbent dosage, and pH. Finally, SBP, SBMAC, and SBMAC2 were prepared and analysed using BET, SEM-EDX, and FTIR to characterise their properties.

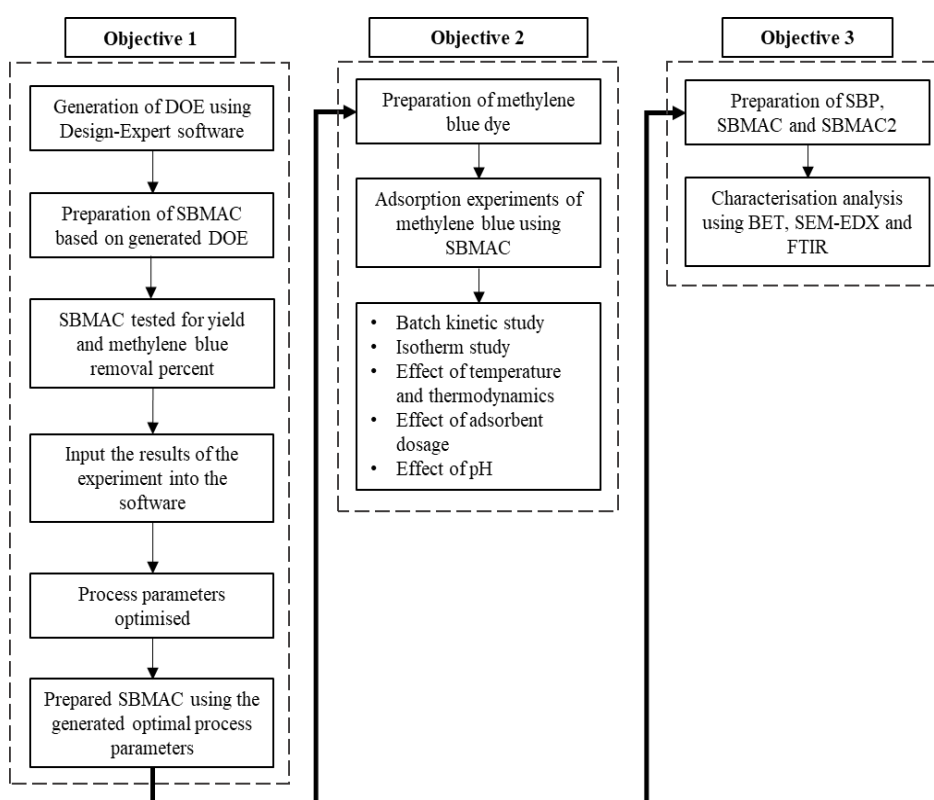


Figure 3.1: Process flow chart of research methodology

3.2 Materials

Three primary materials for the preparation of SBMAC were sago bark, iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and iron (II) sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). Sago bark was used as a precursor biomass material, while $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were used as a magnetic medium for the synthesis of magnetic activated carbon. Potassium hydroxide (KOH) was also used as an activation agent for SBMAC. Sago bark was collected from Shimada Sago Chemical Sdn Bhd, a sago mill located in Dalat, Mukah, Sarawak. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were purchased from HmbG Chemicals. KOH pellet was purchased from J.T. Baker. Methylene blue hydrate ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot x\text{H}_2\text{O}$) was purchased from Sigma-Aldrich and used for a dye adsorption study using SBMAC. Analytical-grade chemicals were employed throughout the study. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) obtained from Merck Millipore were utilized for pH control.

Raw sago bark was cleaned from contamination under running water and sun-dried for a day. The cleaned sago bark was cut into smaller pieces using a saw, cleaned using deionised distilled water to eliminate any contamination and dried in a Memmert universal oven (UF50) for 48 hours at 80°C with 100% fan and 100% flap setting. Dried sago bark was then ground using a Panasonic mixer grinder (MX-AC400TSK) to achieve a particle size range of 0.16 mm to 0.3 mm which segregates using 0.3 mm and 0.16 mm sieve sizes. Prepared sago bark powder (SBP) was stored in an airtight plastic container for the next experiment.

A stock solution of methylene blue (1000 mg/L) was prepared using methylene blue hydrate. A precise amount of 1.0 g of methylene blue hydrate was weighed using a balance and transferred into a 1000 mL volumetric flask. Deionized water was then added

to the flask until the solution reached the calibration line. The volumetric flask was closed with a cap and mixed thoroughly by inverting the flask several times and to ensure the proper homogeneity of the solution, the solution was subsequently stirred using a magnetic stirrer for a duration of 5 minutes. The prepared methylene blue stock solution was stored away from the light to preserve its stability. To dilute the stock solution to the desired concentration, Equation 3.1 was used.

$$C_1 V_1 = C_2 V_2 \quad \text{Equation 3.1}$$

Where, C_1 and C_2 are the concentration of the stock solution and the desired concentration of the solution, respectively. Meanwhile, V_1 and V_2 are the volume of stock solution required and the volume of desired solution, respectively.

The required amount of stock solution was measured and extracted using a pipette and transferred to a volumetric flask. Deionised water was added to the volumetric flask up to the calibration line. The diluted methylene blue solution was mixed thoroughly by inverting the flask several times and further stirred using a magnetic stirrer for 5 minutes. The diluted methylene blue was ready for the next experiment. 0.1 M of NaOH and HCl were also prepared by using the same method as diluted methylene blue solution.

3.3 Experimental Design for Optimisation of Preparation Parameters

The objective of this study was to optimize the preparation parameters for SBMAC using the response surface methodology (RSM) with a Box-Behnken design. The experimental design and data analysis were performed using Stat-Ease Design-Expert 13 software. The preparation parameters considered were the pyrolysis heating temperature ($^{\circ}\text{C}$), impregnation ratio of SBP to Fe(III) and Fe(II), and heating time of pyrolysis (min). A set of 17 experimental runs was generated using the Box-Behnken design, which involves three levels for each factor, as shown in Table 3.1.

Table 3.1: The design of the experiment generated by Design Expert software

Run	Process variables		
	Impregnation ratio, X_1	Pyrolysis temperature, X_2 (°C)	Heating time, X_3 (min)
1	1.50	400	90
2	0.75	400	120
3	0.75	700	120
4	0.00	700	90
5	0.00	550	120
6	0.75	550	90
7	0.75	550	90
8	0.75	550	90
9	0.00	550	60
10	1.50	700	90
11	0.00	400	90
12	1.50	550	120
13	1.50	550	60
14	0.75	550	90
15	0.75	400	60
16	0.75	-700	60
17	0.75	550	90

The pyrolysis heating temperature (°C), impregnation ratio of Fe(III) and Fe(II), and heating time of pyrolysis (min) were varied within the specified ranges, as shown in Table 3.2. The impregnation ratio ranges between 0 to 1.5, pyrolysis temperature ranges between 400 to 700°C, and heating time ranges between 60 to 120 mins. These ranges were selected based on the findings reported in review papers on biomass pyrolysis (Kan et al., 2016; Thines et al., 2017; Wang et al., 2019). The impregnation ratio, which indicates the amount of magnetic medium (Fe(II) and Fe(III)) to SBP, was tested at 0, 0.75, and 1.5 parts of magnetic medium per part of SBP, respectively. The SBP mass was fixed at 10 grammes, while the magnetic medium adjusted based on these ratios. Following the preparation of SBMAC samples using the designed experimental conditions, two response variables were measured: yield of SBMAC, Y_1 (%) and percentage removal of methylene blue, Y_2 (%). The yield of SBMAC was determined by measuring the weight of the

obtained carbon after pyrolysis. The equation used to calculate the yield is shown in Equation 3.2.

Meanwhile, the percentage removal of methylene blue was assessed by quantifying the dye concentration before and after the adsorption process. The data was calculated using Equation 3.3. The experimental conditions of the methylene blue adsorption are shown in Table 3.3 and the conditions were a justified method from past research (Ebadollahzadeh & Zabihim, 2020; Yao et al.,2020). The collected data was then analysed using Design-Expert software, a powerful statistical analysis tool for experimental design and RSM. The software assists in developing a mathematical model that relates the preparation parameters to the response variables. Then, the generated mathematical model was validated by preparing SBMAC using optimal preparation parameters generated from the model. The response variables were then tested using optimal SBMAC prepared to validate the accuracy of the generated mathematical model.

Table 3.2: Three levels of process variables of SBMAC preparation

Process variables	Symbols	Levels		
		-1	0	+1
Impregnation ratios	X_1	0.00	0.75	1.50
Pyrolysis temperature (°C)	X_2	400	550	700
Heating time (min)	X_3	60	90	120

Table 3.3: Experimental conditions for methylene blue adsorption

Adsorption parameters	
Initial concentration of dye	50 mg/L
SBMAC dose	0.1 g/L
Dye pH	6
Contact time	90 mins
Adsorption temperature	303 K
Agitation speed	150 rpm

3.4 Synthesis of Sago Bark Magnetic Activated Carbon (SBMAC)

SBMAC was synthesised by using the optimal preparation parameters obtained from the DOE. 10 g of prepared SBP was immersed with 50 mL of deionised water, 4.58 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.15 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ for 24 hours. After 24 hours, the suspension was ultrasonicated for 4 hours to properly impregnate FeCl_3 and FeSO_4 onto SBP. Ultrasonicated suspension was then filtered using filter paper and dried overnight using an

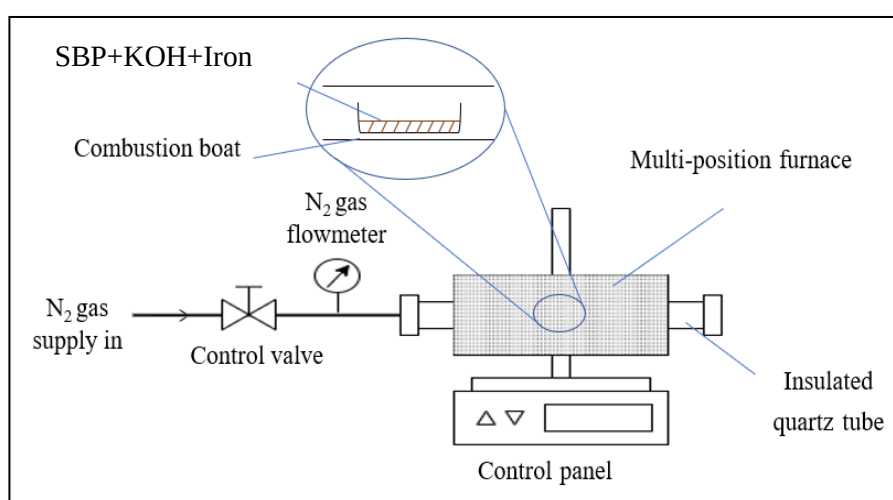


Figure 3.2: Schematic diagram of experimental set-up for SBMAC

oven at 60°C . Subsequently, dried impregnated SBP was ultrasonicated with KOH (1:0.5) for 2 hours for the activation process. Suspension was then filtered and dried using an oven at 60°C to remove any remaining moisture before pyrolysis. Prepared dried impregnated sago bark was stored in a vacuum desiccator before the next experiment.

Impregnated sago bark was pyrolysed using a multi-position tube furnace (BSG-1200X) under an N_2 gas atmosphere. N_2 gas was flowing through the tube furnace at 1 atm and controlled at the lowest flow rate as the tube furnace was smaller compared to the muffle furnace and needed a lower amount of nitrogen gas to keep the furnace environment in an inert state. The impregnated sago bark was placed on a 50 mL alumina combustion

boat. The combustion boat was then inserted into 50 mm OD, 44 mm ID and 450 mm length of quartz tubes. Figure 3.2 shows the schematic diagram of the equipment and process undergone to produce SBMAC.

The sample was heated in a tube furnace with a controlled heating rate of 10°C/min until reaching a temperature of 700°C. The desired temperature was maintained for a duration of an hour. After the reaction process, sago bark magnetic activated carbon was set to cool down at room temperature. SBMAC was weighed to determine the yield of the final product by using Equation 3.2.

$$Yield (\%) = \frac{W_1}{W_0} \times 100 \quad \text{Equation 3.2}$$

Where, W_1 is the dry weight (g) of the final magnetic activated carbon produced and W_0 is the dry weight of the magnetic activated carbon before pyrolysis.

Produced powdered SBMAC, washed using 0.1 M of hydrochloric acid (HCl), and deionised distilled water to control SBMAC pH at pH 7. Washed SBMAC was dried at 60°C in an oven and stored in an airtight container in a vacuum desiccator for the next experiment. SBMAC dried overnight prior to the next experiment at 60°C to avoid any experimental error made due to moisture.

3.5 Adsorbent Characterisation

The samples used for the characterisation study were SBP, SBMAC and SBMAC after the adsorption study (SBMAC2). For SBMAC after the adsorption sample, SBMAC taken was the sample from the effect of dye initial concentration study at 500 mg/L of methylene blue dye was used. Prior to the characterization study, all samples were dried overnight at 60°C to eliminate any potential errors caused by moisture content.

3.5.1 Brunauer-Emmet-Teller (BET)

The surface area of the sample was analyzed using the BET (Brunauer-Emmett-Teller) method with an automated gas sorption analyzer (Quantachrome iQ-07165). The sample was subjected to degassing at a temperature of 180°C for a duration of 3 hours to remove any adsorbed gases or contaminants. This experiment was assisted by a lab technician at UNIMAS. The surface area (m²/g) of the sample was generated using ASiQwin software and further analysed.

3.5.2 Fourier Transform Infrared (FTIR)

Fourier transform infrared (FTIR) is an analysis technique used to identify the functional group of the sample. FTIR analysis was done using a Shimadzu IRAffinity-1S spectrometer. Samples for FTIR analysis were prepared by mixing the sample with potassium bromide (KBr) in a 1:10 ratio by using agate mortar and pestle. The sample was then compressed into a thin pellet using a hand hydraulic press and placed in the sample holder. The instrument was first calibrated and set up for analysis at a wavenumber range of 400 to 4000 cm⁻¹. The sample holder was then inserted into the spectrometer, and the instrument was operated to perform the FTIR analysis. Spectra were generated using IRSolution software, which provides information on the functional groups present in the sample. The data from the IRSolution was extracted and plotted by using Origin 2023b software for a clear image of the spectra and the interpretation of the spectra was done based on the literature of past research.

3.5.3 Scanning Electron Microscopy (SEM) with Energy-dispersive X-ray (EDX)

Scanning electron microscopy (SEM) with Energy-dispersive X-ray spectroscopy analysis was used to obtain images of sample surface morphology and to characterise the

elemental component that is present in the sample. SEM-EDX characterisation of samples was done using a Hitachi tabletop microscope (TM4000Plus II). The magnification, focus, contrast and brightness of the image were adjusted to achieve the 100x, 500x, and 1000x magnification and desired image quality. Using the same image generated at fast mode, EDX analysis was done in Bruker Quantax software which provides the spectrum of surface elemental composition information of the sample. SEM and EDX data were saved in image and MS Word format, respectively.

3.6 Adsorption Experiments

An adsorption study was conducted to study the adsorption capability of SBMAC on dye. The dye used to determine SBMAC dye adsorption capability was methylene blue. The adsorption performance of SBMAC on methylene blue was tested in a batch process under different adsorption parameters (adsorbent dose, pH of the medium, adsorption temperature, contact time and methylene blue initial concentration) to study the kinetic, isotherm and the effect of each adsorption parameter.

3.6.1 Kinetic Study

3.6.1.1 Batch kinetics at different initial concentrations of dye

Batch kinetic experiments were carried out using varying initial concentrations of methylene blue to determine the optimal contact time for achieving maximum adsorption efficiency. Additionally, these experiments aimed to evaluate the adsorption capacity of SBMAC at different methylene blue concentrations. The data from this experiment was also used to analyse the kinetic model of methylene blue adsorptions. Batch experiments were done in a 250 ml conical flask containing four different concentrations (100, 200, 300 and 500 mg/L) of 100 mL of methylene blue solution where 0.1 g/L of SBMAC was added and shaken in a water bath shaker (Memmert WNB45) at 150 rpm for 24 hours. The

methylene blue solution was diluted to the desired concentration using the method explained in Section 3.2. The pH of the dye solution was adjusted to pH 6 by adding 0.1M NaOH and 0.1M HCl. The temperature of the water bath shaker was set to 303 K. Experimental conditions, including pH, temperature, and other relevant details, are summarized in Table 3.4. To assess the impact of contact time on the interaction between SBMAC and the methylene blue solution, 5 mL of the sample was extracted at specified time intervals using a micropipette. The SBMAC adsorbent was then separated from the solution using a strong magnet and filter paper, allowing for accurate determination of the sample concentration. The sample concentration was diluted and transferred to the cuvette. Six different concentrations of methylene blue were diluted from the same stock solution to generate a standard curve with concentrations ranging from 1 to 5 mg/L. The cuvette containing the sample and standard methylene blue solutions was placed in UV Spectrophotometer (Shimadzu UV-1800). The photometer's wavenumber was adjusted to 660 nm to measure the final concentration of the methylene blue solution. This value was then compared to the initial concentration to determine the adsorption efficiency of SBMAC. The adsorption efficiency of methylene blue was determined by Equation 3.3,

$$\text{Adsorption efficiency (\%)} = \frac{C_0 - C_e}{C_e} \times 100 \quad \text{Equation 3.3}$$

Where, C_0 is methylene blue initial concentration (mg/L) while, C_e is methylene blue concentration at equilibrium (mg/L).

Meanwhile, the adsorption capacity of SBMAC was determined by Equation 3.4,

$$\text{Adsorption capacity, } q_e (\text{mg/g}) = \frac{V}{m} (C_0 - C_e) \quad \text{Equation 3.4}$$

Where, V is the volume of methylene blue solution (L), and m is the mass of SBMAC added into the system (g).

Table 3.4: Experimental conditions for the effect of contact time and initial concentration of methylene blue

Adsorption parameters	
Initial concentration of dye	100, 200, 300 and 500 mg/L
SBMAC dose	0.1 g/L
Dye pH	6
Contact time	1440 mins
Adsorption temperature	303 K
Agitation speed	150 rpm

3.6.1.2 Kinetic modelling

The objective of this study was to investigate the kinetics of methylene blue adsorption using SBMAC through the application of various kinetic models, including the Pseudo-first-order (PFO), Pseudo-second-order (PSO), and Intraparticle diffusion (ID) models. The concentration over time data from section 3.4.1 was used for the kinetic modelling. The PFO model was analysed using Origin 2023B software, while the PSO and ID models were analysed using Excel. Due to the inaccuracy of the PFO model linear fitting, Origin 2023B was used to analyse the non-linear fitting of the PFO model. The PFO model was analysed using Equation 2.1. Non-linear graphs of time q_t versus t were plotted for four different methylene blue concentrations. The graph was then examined using the Box-Lucas1 non-linear fitting model, which has the same modelling features as the PFO model. The y-intercept, gradient, and regression of the models were then developed to determine the equilibrium adsorption capacity of SBMAC and PFO rate constant. Meanwhile, the linearisation equation of PSO, provided in Equation 2.2, was

used to analyse the PSO model. The linear graph of t/q_t against time was plotted for four different concentrations of methylene blue. The LINEST function in Excel was used to determine the model's linear function to determine the equilibrium concentration, PSO rate constant, and SBMAC sorption rate. Additionally, the ID model was analysed by plotting the adsorption capacity of SBMAC versus the square root of time. The plot was evaluated using the linearised Weber and Morris ID kinetic model from Equation 2.5. In contrast to the PSO and PFO models, the plots were examined for the presence of several linear segments showing the involvement of different diffusion processes and the rate constant of each diffusion was calculated. The kinetics data and model analysis reveal important details about the rate-controlling steps and mechanism of methylene blue adsorption on SBMAC.

3.6.2 Isotherm Study

The objective of this study was to investigate the adsorption isotherms of methylene blue using SBMAC by applying several isotherm models, including the Langmuir, Freundlich, Temkin, and Dubinin-Raduskevich (DR) models. Batch adsorption experiments were conducted by adding 50 mL of different concentrations of methylene blue solutions to separate 150 mL conical flask containing a fixed dosage of SBMAC. The mixtures were agitated for 24 hours to establish adsorption equilibrium. After 24 hours, SBMAC was separated from the mixture using a strong magnet and filter paper. After the separation process, the equilibrium concentration of methylene blue after adsorption was measured using a spectrophotometer. The collected data was then used for isotherm model analysis. The experimental conditions of the isotherm study are tabulated in Table 3.5.

Table 3.5: Experimental conditions for isotherm model analysis

Adsorption parameters	
Initial concentration of dye	80 – 500 mg/L
SBMAC dose	0.1 g/L
Dye pH	6
Contact time	1440 mins
Adsorption temperature	303 K
Agitation speed	150 rpm

All data were computed as linear models using Excel. For the analysis of the Langmuir isotherm model, the experimental data was plotted as a graph of C_e/q_e against C_e , where q_e was calculated using Equation 3.4 and C_e was the concentration of methylene after 24 hours of adsorption. From the model, maximum adsorption capacity, Langmuir isotherm constant, and adsorption separation factor can be estimated. Meanwhile, the Freundlich model was plotted as a linear graph of $\log q_e$ against $\log C_e$. From the model, Freundlich isotherm parameters were calculated. The Temkin model was analysed by plotting q_e against $\ln C_e$, and the DR model was analysed by plotting $\ln q_e$ against ε^2 , where ε represents the Polanyi potential. The obtained plots were assessed for linearity, and the model parameters were calculated accordingly. The isotherm model analysis allows for a better insight into the adsorption behaviour of methylene blue on SBMAC, providing information into the adsorption capacity, surface heterogeneity, and energetics of the adsorption process.

3.6.3 Effect of Temperature and Adsorption Thermodynamics

The objective of this study is to examine the impact of temperature on the adsorption of methylene blue using SBMAC and to explore the associated thermodynamic aspects of the adsorption process. The temperature effect and adsorption thermodynamics can provide a valuable understanding of the adsorption mechanism and process feasibility.

This experiment was done by varying the temperature of the adsorption system from 303 K to 333 K. The temperature of the adsorption system was controlled by adjusting the temperature control panel on the water bath shaker. Each experiment was conducted separately for each adsorption temperature for 90 minute.

Table 3.6: Experimental conditions for the effect of temperature experiments

Adsorption parameters	
Initial concentration of dye	100 mg/L
SBMAC dose	0.1 g/L
Dye pH	6
Contact time	90 mins
Adsorption temperature	303, 313, 323 and 333 K
Agitation speed	150 rpm

The details of experimental conditions were tabulated in Table 3.6. On the other hand, the data from the effect of temperature experiments were used to determine the thermodynamics parameters by applying the Van't Hoff equation as discussed in section 2.4.3. The thermodynamics parameters calculated, include the standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0).

3.6.4 Effect of Adsorbent Dosage

The objective of this research was to investigate the impact of SBMAC dosage on the adsorption process of methylene blue. By studying the effect of SBMAC dosage, valuable insights can be gained regarding the optimal dosage required for the effective adsorption of methylene blue. This study was done in a batch process where different amounts of SBMAC were used for methylene blue adsorption. 0.0025 g, 0.005 g, 0.025 g, 0.05 g, and 0.1 g of SBMAC were weighed and added into the conical flasks containing 50 mL of methylene blue solutions. The details of experimental conditions are shown in Table

3.7. The experimental data were analysed using Equations 3.3 and 3.4 to assess the influence of adsorbent dosage on the adsorption of methylene blue.

Table 3.7: Experimental conditions for the effect of SBMAC dosage experiments

Adsorption parameters	
Initial concentration of dye	50 mg/L
SBMAC dose	0.05, 0.1, 0.5, 1.0 and 2.0 g/L
Dye pH	6
Contact time	90 mins
Adsorption temperature	303 K
Agitation speed	150 rpm

3.6.5 pH of the Point of Zero Charge (pH_{PZC}) of SBMAC and the Effect of pH

The objective of this study is to determine the pH of the point of zero charge (pH_{PZC}) of SBMAC, as well as to investigate the influence of pH on the adsorption of methylene blue using SBMAC. The pH of the point of zero charge (pH_{PZC}) for SBMAC was determined using the pH drift method. 50 mL of 0.01M of NaCl was prepared and the pH was adjusted at a range of pH 3 to 11 by adding HCl and NaOH. These solutions were boiled to minimise CO₂ content. 10 mg of SBMAC was then added to the solutions and agitated at 150 rpm for 24 hours. The final pH of each solution was measured using pH meter. The final and initial pH graph was plotted and the pH_{PZC} was identified as the point where the graphs intersect.

Batch adsorption experiments were conducted using varying pH levels of the methylene blue solution, achieved by adjusting with 0.1 M NaOH and 0.1 M HCl. The pH range selected for the study was from pH 2 to pH 11. Each experiment consisted of adding 0.1 g/L of SBMAC to separate conical flasks containing 50 mL of methylene blue solution with an initial concentration of 100 mg/L, followed by a 90-minute adsorption period. The

water bath temperature was controlled at 303 K, and agitation was set at 150 rpm. After 90 minutes, SBMAC was separated from the solution using a magnet and filter paper. Further details regarding the experimental conditions can be found in Table 3.8. The final concentration of methylene blue in the solution was determined using a spectrophotometer, while the final pH was measured using a pH meter. The adsorption capacity of SBMAC at different pH values was calculated based on these measurements. The collected data was then analyzed to evaluate the impact of pH on the adsorption of methylene blue.

This analysis provides insights into the adsorption mechanism and helps identify the optimal pH range for efficient removal of methylene blue using SBMAC. The experiment was repeated for accuracy, the results were averaged, and the pH_{pzc} value was interpreted, providing valuable insights into the SBMAC surface charge properties crucial for various applications.

Table 3.8: Experimental conditions for effect of pH

Adsorption parameters	
Initial concentration of dye	100 mg/L
SBMAC dose	1.0 g/L
Dye pH	2, 3, 4, 5, 6, 7, 8, 9, 10 and 11
Contact time	90 mins
Adsorption temperature	303 K
Agitation speed	150 rpm

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Experimental Design for Optimisation of Preparation Parameters

This analysis relies on the Design-Expert 13 software and implements the desirability approach for the determination of the optimal values of process parameters (impregnation ratio, pyrolysis temperature, and heating time) involved in the preparation of SBMAC. Based on the limits in Table 3.2, the design of experiments was generated by Design-Expert, and the experiments were conducted. There are a total of 17 sets of runs generated. The results from the experiments were key-in to the table in Design-Expert and extracted as shown in Table 4.1. After all experimental data was added to the table, the predicted data was generated based on the models developed from the experimental data. The Actual vs. Predicted SBMAC yield and methylene blue removal graph were generated and extracted from the software, as shown in Figure 4.1. The straight line is the predicted graph, while the experimental data is the scattered point around the line. Based on the experimental results, the highest SBMAC yield of 56.91% was obtained at the lowest pyrolysis temperature limit, the lowest heating time limit, and the 0.75 impregnation ratio. Meanwhile, the highest methylene blue removal of 99.87% was obtained at the highest pyrolysis temperature limit, the highest impregnation ratio limit, and 90 minutes of heating time.

Table 4.1: Actual and predicted values of SBMAC yield and methylene blue removal responses

Run	Process variables			Response values			
	X ₁	X ₂ (°C)	X ₃ (min)	SBMAC yield, Y ₁ (%)		Methylene blue removal, Y ₂ (%)	
				Actual	Predicted	Actual	Predicted
1	1.50	400	90	56.81	57.71	80.03	80.32
2	0.75	400	120	52.16	52.10	75.53	74.53
3	0.75	700	120	38.09	39.10	89.22	91.35
4	0.00	700	90	25.81	24.91	99.74	98.25
5	0.00	550	120	28.47	28.37	87.15	85.80
6	0.75	550	90	39.09	39.09	88.95	89.29
7	0.75	550	90	39.09	39.09	88.95	89.29
8	0.75	550	90	39.09	39.09	88.95	89.29
9	0.00	550	60	34.16	35.00	87.59	86.48
10	1.50	700	90	39.91	39.75	99.87	97.14
11	0.00	400	90	35.84	36.01	79.21	81.43
12	1.50	550	120	51.82	50.99	79.85	80.08
13	1.50	550	60	48.81	48.92	89.51	89.98
14	0.75	550	90	39.09	39.09	88.95	89.29
15	0.75	400	60	56.91	55.91	81.30	79.82
16	0.75	700	60	39.80	39.85	94.51	96.64
17	0.75	550	90	39.09	39.09	88.95	89.29

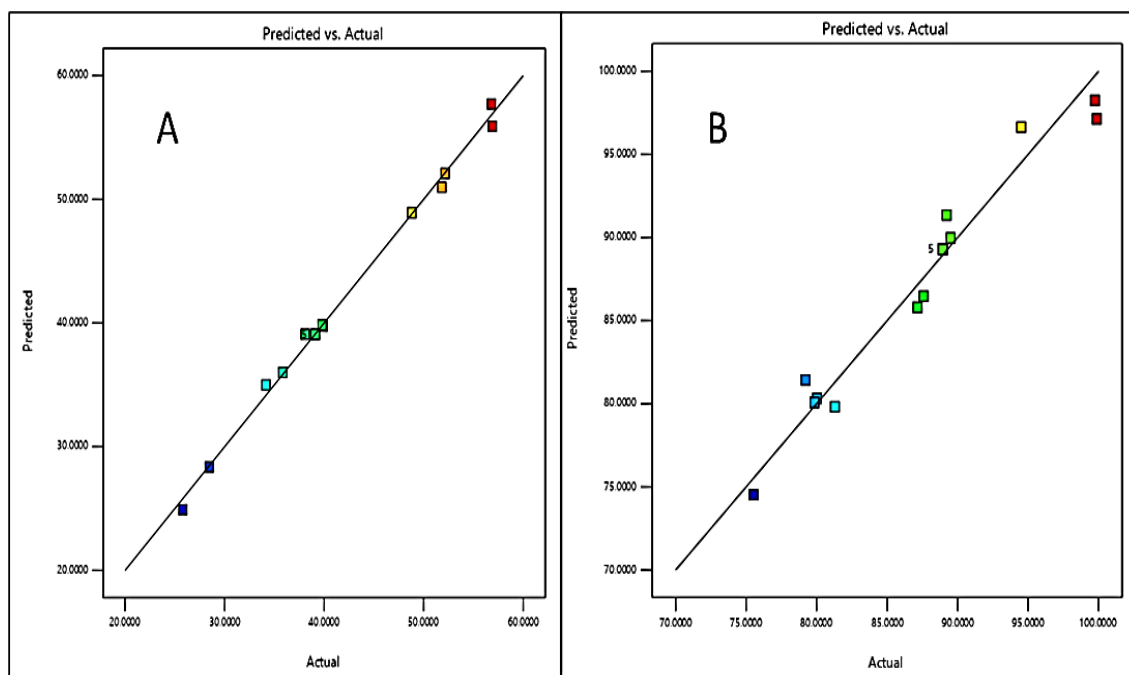


Figure 4.1: Predicted vs actual data plot of SBMAC yield (A) and methylene blue removal (B)

Based on the predicted and actual data, the perturbation graph of both responses was generated to analyse the main effects of each process variable. Figure 4.2 shows the generated perturbation graph of SBMAC yield and methylene blue removal. As shown in Figure 4.2, the impregnation ratio (A) shows an increasing trend for the effect of SBMAC yield because addition of metal salts FeCl_3 and FeSO_4 to biomass before pyrolysis acts as a catalyst, enhancing the conversion of biomass into activated carbon and increasing the overall carbon yield compared to non-impregnated biomass (Xia et al., 2023). Conversely, the pyrolysis temperature (B) exhibits a decreasing trend for the effect of SBMAC yield, as higher temperature generally reduces the yield of activated carbon and promoting the conversion of biomass into volatile compound and gases (Duan et al., 2021). On the other hand, the heating time (C) has a relatively small impact on SBMAC yield in comparison to impregnation ratio and pyrolysis temperature. Shorter heating times typically result in higher yield since more degradation happens during pyrolysis as progresses. However, the

heating time is normally determined by the pyrolysis temperature in order to influence carbon yield production (Duan et al., 2021). Therefore, while heating time has an effect on yield, it has a small effect than the impregnation ratio and pyrolysis temperature, making it less significant for optimising the overall yield of SBMAC.

On the contrary, impregnation ratio, pyrolysis temperature and heating time affect methylene blue removal from SBMAC yield differently. The increase in pyrolysis temperature (B), increases the percent removal of methylene blue, while the increase in impregnation ratio (A) and heating time (C) slightly lower the efficiency of SBMAC to

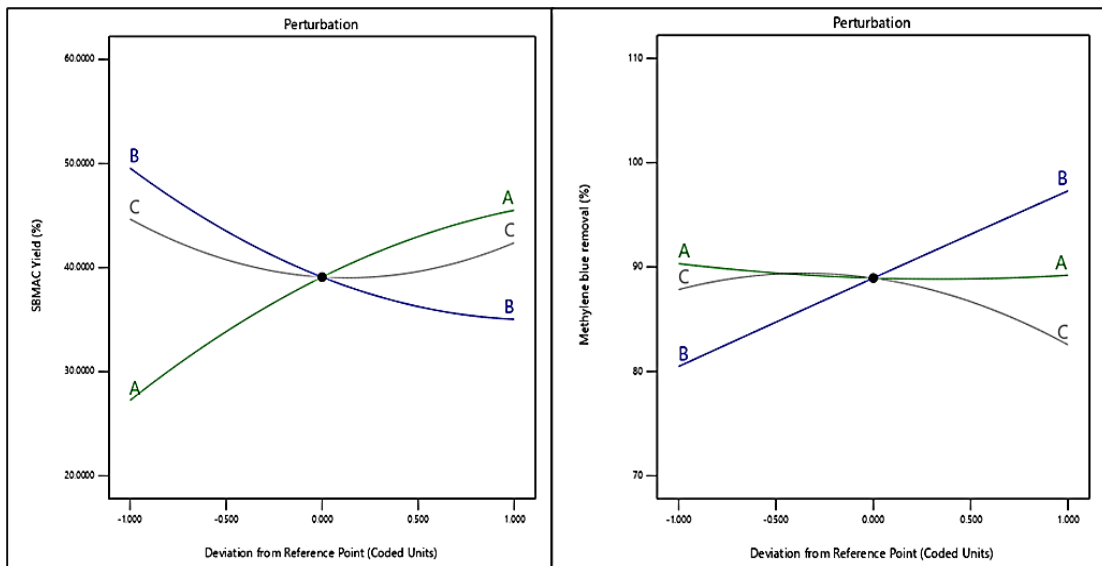


Figure 4.2: Perturbation of SBMAC yield and methylene blue removal

remove methylene blue. The adsorption of methylene blue by SBMAC was highly affected by the porosity of the adsorbent. This is supported by a study conducted by Borghei et al. (2021), which found that pyrolysis temperature has a substantial impact on activated carbon adsorption capacity on methylene blue since increasing the activation temperature promotes the formation of micropores on the adsorbent's surface. The perturbation plot correlates with experimental data of the highest SBMAC yield and methylene blue removal.

Apart from the main effect of the process variable, the effects of the interaction of main variables were also analysed using the generated 3D graph shown in Figures 4.3 and 4.4. AB is the interaction between the impregnation ratio and pyrolysis temperature, AC is the interaction between impregnation ratio and heating time, and BC is the interaction between pyrolysis temperature and heating time. The effects of process variables' interaction on SBMAC yield were discussed. For the interaction of AB, the highest SBMAC yield was obtained at the lowest temperature limit and the highest impregnation limit. The yield of SBMAC at this interaction is recorded at 56.8086%. Meanwhile, the lowest SBMAC yield recorded during AB interaction is 25.8057%, where the impregnation ratio and pyrolysis temperature are 0 and 700°C, respectively. Therefore, the impregnation ratio affects the yield positively, while pyrolysis temperature negatively affects the yield.

However, the same AB interaction levels generate an average SBMAC yield of 39.0940%, 39.9143% and 35.8443% for mid, high, and low levels, respectively. On the other hand, the highest SBMAC yield recorded for AC interaction is 51.8243%, where the impregnation ratio and heating time are the highest at 1.5 and 120 minutes, while the lowest SBMAC yield recorded during this interaction is when the impregnation ratio is 0 and heating time is at 120 minutes. The effect of the impregnation ratio is positively significant, but the effect of heating time is very minimal as both long heating times produce the highest and lowest yield for AC interaction. As for BC interaction, the highest yield recorded is 56.9114%, while the lowest yield recorded is 38.0940%. The highest yield during this interaction was obtained at the lowest pyrolysis temperature of 400°C and heating time at 60 minutes, while the lowest was obtained at the highest levels of interactions when pyrolysis temperature is 700°C and heating time is 120 minutes. The

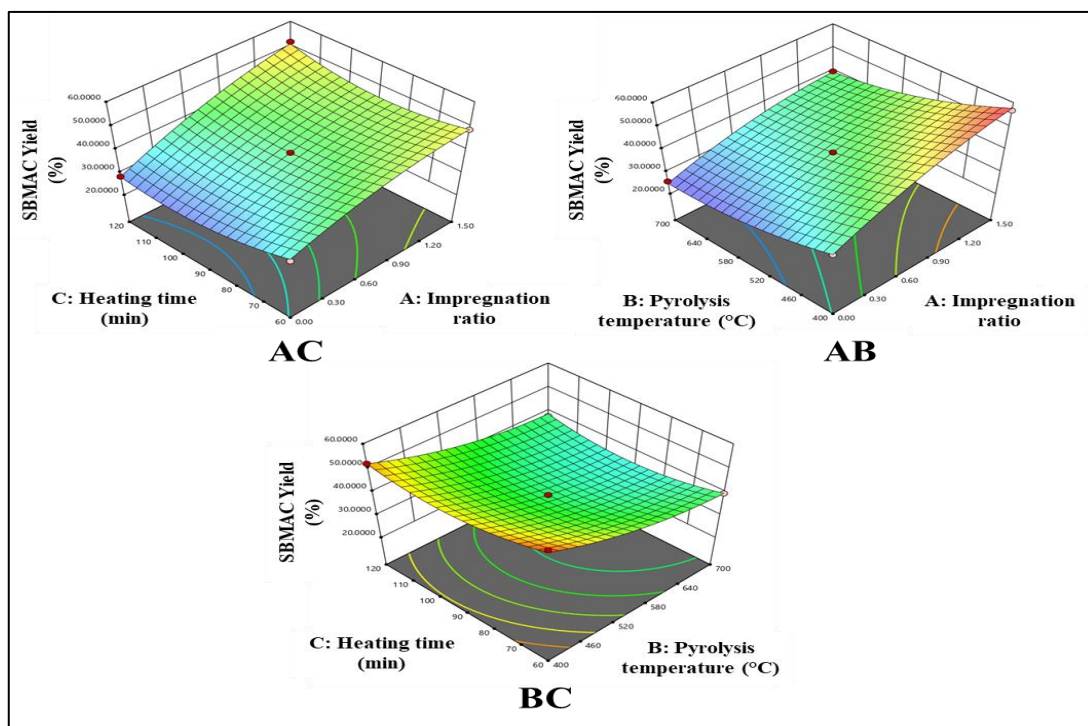


Figure 4.3: 3D graph of the effect of process variables interaction on SBMAC yield

increase of BC interactions show a negative effect on the yield of SBMAC. Despite that, the lowest yield recorded for this interaction is higher than that recorded during AB and AC interactions. Also, the mid-level of all three interactions generated the same yield of SBMAC of 39.0940%. The highest SBMAC yield was recorded during the lowest level of BC interactions, where pyrolysis temperature is 400°C and heating time is 60 minutes, and the lowest yield was recorded during the low and high levels of AB interactions, where impregnation ratio is 0 and pyrolysis temperature is 700°C.

The 3D interactions of process variables vs methylene blue removal were plotted as shown in Figure 4.4. From the graph of AB interactions, the highest methylene removal, 99.87%, was recorded at the highest level of impregnation ratio and pyrolysis temperature. In comparison, the lowest removal of methylene, 79.212%, was recorded at the lowest level of process variables. Hence, these interactions yielded a positive effect on methylene

blue removal. On the other hand, for AC interactions, the highest methylene blue removal was recorded at 89.5073%, while the lowest was at 79.846%.

The highest removal percent was recorded at the high impregnation ratio level and a low heating time level. The difference between the highest and the lowest methylene blue removal for this interaction is the lowest compared to the other interactions. This is consistent with the perturbation plot of impregnation ratio and heating time effects on methylene blue removal, where variations in A and C have only a small influence on the effectiveness of SBMAC for methylene blue removal. For BC interactions, the highest methylene blue removal was recorded at 94.5138%, while the lowest was at 75.5284%.

The highest removal for this interaction was recorded at the highest level of temperature and the shortest level of heating time, while the lowest recorded removal was recorded at the lowest level of pyrolysis temperature and the longest level of heating time.

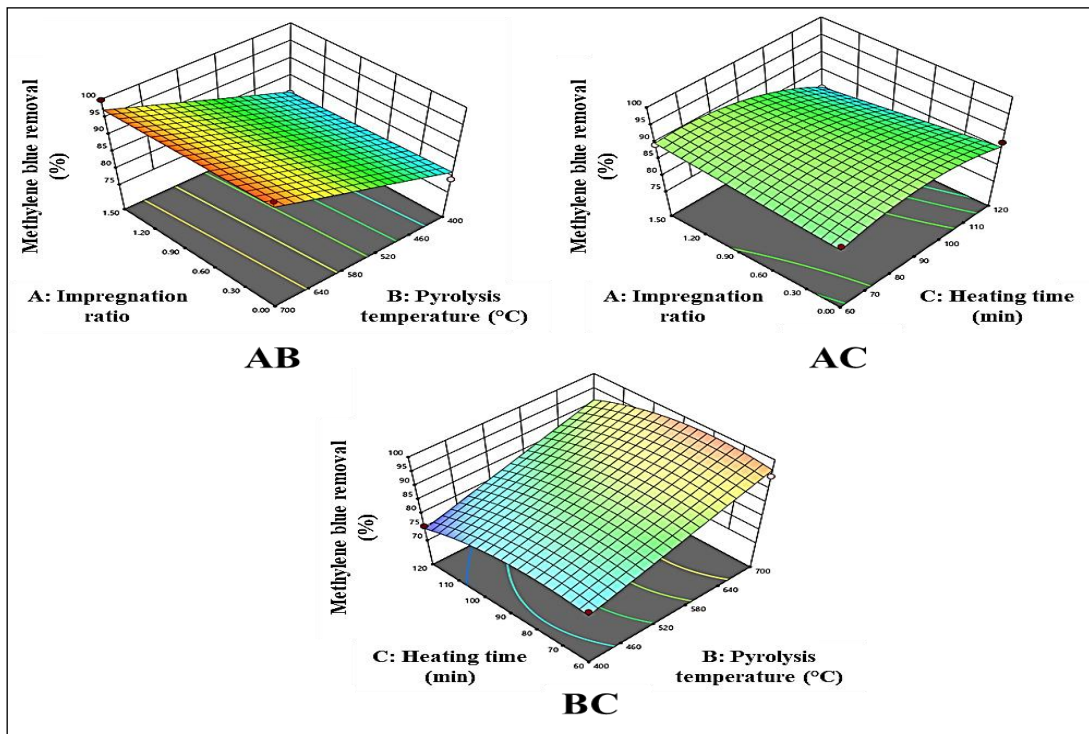


Figure 4.4: 3D graph of the effect of process variables interaction on methylene blue removal

The difference between the highest and lowest percent removal of methylene from this interaction is 18.9854% due to the significant impact of B on the adsorption ability of SBMAC. In brief, the increase of pyrolysis temperatures increases the ability of SBMAC to adsorb methylene blue, while the impregnation ratio and heating time only slightly impact the ability of SBMAC for methylene blue adsorption.

4.1.1 SBMAC Yield Model

The quadratic model for SBMAC yield response was developed based on the Box-Behnken Design model and shown as Equation 4.1. Also, the analysis of variance (ANOVA) of the developed mathematical model was generated and shown in Table 4.2.

$$Y_1 (\%) = 149.0209 + 19.0899 X_1 - 0.2092 X_2 - 1.0907 X_3 - 0.0152 X_1 X_2 + 0.0967 X_1 X_3 + 0.0002 X_2 X_3 - 4.8212 X_1^2 + 0.0001 X_2^2 + 0.0049 X_3^2 \quad \text{Equation 4.1}$$

Based on Table 4.2, the SBMAC yield model is deemed significant because the calculated p-value is less than 0.0001. The computed F-value is 195.87, with a 0.01% probability of being caused by noise. In addition, the lack of fit is regarded as insignificant because the p-value of the model is less than 0.05. On the other hand, the significance of each process parameter and its interactions were also examined using the p-value. Any process parameters and interactions with a p-value larger than 0.10 is considered insignificant. Based on the analysis, A, B, and C² are the most significant process parameters affecting the yield of SBMAC preparation with the same p-value of less than 0.0001. Also, other process variables and the interactions are considered significant except BC interaction, as the p-value obtained is 0.1176. However, the model does not need to be simplified to enhance the overall model because it would not significantly impact the precision of the model as only one insignificant parameter was obtained.

Table 4.2: ANOVA for quadratic model of SBMAC yield

Source	Sum of squares	Mean square	F-value	p-value	Statistics
Model	1288.06	143.12	195.87	< 0.0001	Standard deviation: 0.8548 Mean: 41.42 Coefficient of variation: 2.06% PRESS: 81.84 R ² : 0.9960 Adjusted R ² : 0.9910 Predicted R ² : 0.9367 Adequate precision: 50.0242
A – Impregnation ratio	667.46	667.46	913.45	< 0.0001	
B – Pyrolysis temperature	422.12	422.12	577.70	< 0.0001	
C – Heating time	10.41	10.41	14.25	0.0069	
AB	11.75	11.75	16.08	0.0051	
AC	18.92	18.92	25.90	0.0014	
BC	2.33	2.33	3.18	0.1176	
A ²	30.97	30.97	42.38	0.0003	
B ²	43.42	43.42	59.42	0.0001	
C ²	82.82	82.82	113.35	< 0.0001	
Residual	5.11	0.7307			
Lack of fit	5.11	1.70			

The statistics of the SBMAC yield model are also determined and included in Table 4.2. It includes the standard deviation, mean, coefficient of variation, predicted residual errors of squares (PRESS), R², adjusted R², predicted R², and adequate precision. The standard deviation of the model explained the deviation of the experimental data from the predicted values based on the developed model. The standard deviation of the model is calculated at 0.8548 and considered low, which is preferred since it indicates that the experimental data does not deviate too far from the predicted data. The mean is the average value of the SBMAC yield, which is 41.42%. The coefficient of variation has a similar purpose as the standard deviation, but considering the mean of the SBMAC yield values, which is calculated at 2.06%. PRESS is also determined to have a low value of 81.84. As for R², adjusted R², and predicted R², it is calculated at 0.996, 0.991, and 0.9367, respectively. The values of all regression coefficients are close to 1, indicating the high accuracy of response value prediction. Also, the difference between adjusted R² and predicted R² is 0.0543, which is lower than 0.2, indicating the reasonable agreement between both regression coefficients. Meanwhile, adequate precision is the calculated

signal-to-noise ratio, which should be greater than 4. The value of adequate precision of the SBMAC yield model is 50.0242, indicating the tolerable signal.

4.1.2 Methylene Blue Removal Model

The quadratic methylene blue removal response model was developed based on the same design model as the SBMAC yield response and is shown in Equation 4.2. Also, the ANOVA of the developed mathematical model was generated and shown in Table 4.3.

$$Y_2 (\%) = 26.6675 + 7.1136 X_1 + 0.0577 X_2 + 0.7235 X_3 - 0.0015 X_1 X_2 + 0.1025 X_1 X_3 + 0.00003 X_2 X_3 + 1.4686 X_1^2 - 0.000003 X_2^2 - 0.0042 X_3^2 \quad \text{Equation 4.2}$$

Based on Table 4.3. the SBMAC yield model is deemed significant because the calculated p-value is 0.0004, and the calculated F-value is greater than the p-value. On the other hand, the significance of each process parameter and its interactions were also examined using the p-value. Any process parameters and interactions with a p-value larger than 0.05 is considered insignificant. Based on the analysis, only B, C, and C² are significant because the p-value is less than 0.05, while the other process parameters and interactions are insignificant. Also, the PRESS calculated is high at 444.54, and the difference between adjusted R² and predicted R² is greater than 0.2, which is unreasonable. Thus, a model reduction is required by eliminating the insignificant process factor and interaction based on the p-value of each factor to increase the precision of the model. The ANOVA of the reduced quadratic model of methylene blue removal is shown in Table 4.4, and the reduced quadratic model of methylene blue removal is shown in Equation 4.3.

Table 4.3: ANOVA for quadratic model of methylene blue removal

Source	Sum of squares	Mean square	F-value	p-value	Statistics
Model	706.71	78.52	19.78	0.0004	Standard deviation: 1.99 Mean: 87.54 Coefficient of variation: 2.28% PRESS: 444.54 R ² : 0.9622 Adjusted R ² : 0.9135 Predicted R ² : 0.3948 Adequate precision: 16.2855
A – Impregnation ratio	2.47	2.47	0.6230	0.4558	
B – Pyrolysis temperature	565.85	565.85	142.56	< 0.0001	
C – Heating time	55.98	55.98	14.10	0.0071	
AB	0.1173	0.1173	0.0296	0.8683	
AC	21.25	21.25	5.36	0.0539	
BC	0.0561	0.0561	0.0141	0.9087	
A ²	2.87	2.87	0.7240	0.4230	
B ²	0.0148	0.0148	0.0037	0.9530	
C ²	59.11	59.11	14.89	0.0062	
Residual	27.78	3.97			
Lack of fit	27.78	9.26			

$$Y_2 (\%) = 26.6888 + 8.4792 X_1 + 0.0561 X_2 + 0.7295 X_3 - 0.1025 X_1 X_2 - 0.0041 X_3^2$$

Equation 4.3

As shown in Equation 4.3, only significant variables are included in the model, which was analysed again using ANOVA, as shown in Table 4.4. After reducing the model, the p-value of the model decreased from 0.0004 to less than 0.0001, and F-value increased from 19.78 to 50.21. Thus, lack of fit is considered insignificant. As for the significance of each parameter, pyrolysis temperature is the most significant process parameter affecting the methylene blue removal percentage, with a calculated p-value of less than 0.0001. The impregnation ratio is considered insignificant with a p-value of 0.3677 but is included in the model to maintain the hierarchy of the model.

Table 4.4: ANOVA for reduced quadratic model of methylene blue removal

Source	Sum of squares	Mean square	F-value	p-value	Statistics
Model	703.66	140.73	50.21	< 0.0001	Standard deviation: 1.67 Mean: 87.54 Coefficient of variation: 1.91% PRESS: 91.82 R ² : 0.9580 Adjusted R ² : 0.9389 Predicted R ² : 0.8750 Adequate precision: 23.8543
A – Impregnation ratio	2.47	2.47	0.8823	0.3677	
B – Pyrolysis temperature	565.85	565.85	201.88	< 0.0001	
C – Heating time	55.98	55.98	19.97	0.0009	
AC	21.25	21.25	7.58	0.0188	
C ²	58.11	58.11	20.73	0.0008	
Residual	30.83	2.80			
Lack of fit	30.83	4.40			

The statistics of the reduced quadratic methylene blue removal model are also determined and included in Table 4.4. It includes the standard deviation, mean, coefficient of variation, predicted residual errors of squares (PRESS), R², adjusted R², predicted R², and adequate precision. The standard deviation of the reduced model is calculated at 1.67, decreasing from 1.99 in the initial model, which shows that the deviation predicted response with experimental data of the reduced model is lower than the initial model. Also, the reduced and initial model's mean maintains 87.54% methylene blue removal percent because the data used to calculate the mean is from the experimental data. The coefficient of variation and PRESS also dropped from 2.28% to 1.91% and 444.54 and 91.82, respectively.

As for R², adjusted R², and predicted R², it is calculated at 0.958, 0.9389, and 0.8750, respectively for the reduced model. The value of R² slightly dropped from 0.9622 to 0.958, while the value of adjusted R² increased by 0.0254. Also, predicted R² significantly increased from 0.3948 to 0.8750, resulting in the difference between predicted R² and adjusted R² less than 0.2. Thus, it indicates the reasonable agreement between both regressions, which is not achieved in the initial model. The value of adequate precision of

the initial and reduced methylene blue removal model are 16.2855 and 23.8543, indicating both models have the tolerable signal as both values is greater than 4.

4.1.3 Optimisation of SBMAC Preparation Parameters

The desirability approach was applied to determine the optimum operating conditions. The desired maximum goal values as well as the importance level of the process and response variables are included in the table of constraints for the optimisation, as shown in Table 4.5. The lower and upper limits of process variables were the same as those set for the experiment design. In comparison, the lower and upper limits for the response variables were set based on the minimum and maximum values of experimental data. The optimisation goal is set to maximise the response variables while maintaining the range of the process variables.

Table 4.5: Table of constraints

Name	Goal	Lower limit	Upper limit	Importance
A: Impregnation ratio	is in range	0	1.5	3
B: Pyrolysis temperature	is in range	400	700	3
C: Heating time	is in range	60	120	3
SBMAC Yield (%)	maximise	25.8057	56.9114	5
Methylene blue removal (%)	maximise	75.5284	99.87	5

Based on the constraints set on the experiment's parameters, the optimal operating conditions were selected from 113 starting points, and 51 solutions were generated with the highest desirability value of 0.709, as shown in Table 4.6. The optimal process variables for the preparation of SBMAC were calculated at an impregnation ratio of 1.5, pyrolysis temperature of 700°C, and heating time of 60 minutes. According to the optimal conditions, the projected response variable values for SBMAC yield and methylene blue removal are 42.388% and 98.481%, respectively.

Table 4.6: Optimum values of the process variable and predicted values of the response variables

Name	Optimum values	Name	Predicted values
Impregnation ratio	1.5	SBMAC yield	42.388%
Pyrolysis temperature	700°C	Methylene blue removal	98.481%
Heating time	60 minutes		

The predicted value of response variables was confirmed by preparing SBMAC using the optimal conditions of process variables. Also, the methylene blue removal response was tested using the prepared SBMAC. Both experiments were done in triplicate. Table 4.7 shows the statistical analysis of actual and predicted data. The predicted mean of SBMAC yield is 42.3881%, and the experimental mean is determined at 41.9533%. On the other hand, the predicted mean of methylene blue removal is 98.4804%, and the experimental mean is 98.9333%, slightly higher than the predicted mean. Both response variables were within the 95% low and high prediction interval, confirming the models' prediction. Also, the standard deviation and standard error prediction of SBMAC yield and methylene blue removal actual results and predicted are considered low, meaning the actual data did not deviate far from the prediction. Considering the limitations of actual operating conditions, certain differences occur between the experimental and predicted values; however, the responses still reach a significant value under these conditions. These results indicate that the BBD method and optimisation with desirability functions could be effectively used to optimise the preparation of SBMAC.

Table 4.7: Confirmation of predicted response variables

Statistics	Analysis	
	SBMAC Yield	Methylene blue removal
Predicted mean	42.3881%	98.4804%
Standard deviation	0.8543	1.9923
Standard error prediction	1.1132	2.5944
95% prediction interval low	39.7559%	92.3457%
Data mean	41.9533%	98.9333%
95% prediction interval high	45.0203%	104.6151%

4.2 Synthesis of Sago Bark Magnetic Activated Carbon (SBMAC)

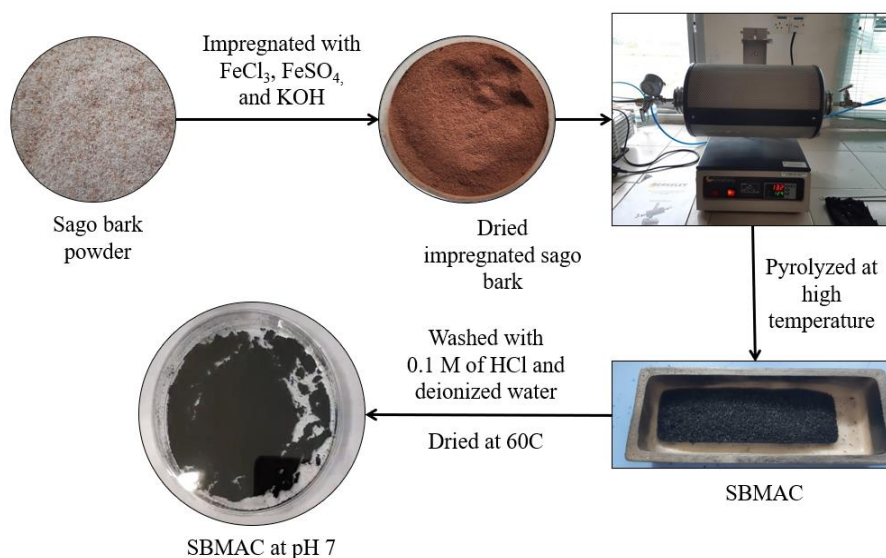


Figure 4.5: Process diagram of SBMAC synthesis

Figure 4.5 shows the SBMAC synthesis process, where SBMAC was successfully produced utilising sago bark as the primary raw material. SBMAC was synthesis based on the optimum values of preparation parameters obtained in Section 4.1.3. Sago bark was ground into a fine powder with a particle size of less than 0.3 mm. Sago bark powder (SBP) that was initially light brown becomes dark brown after being impregnated with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and KOH . Following SBP impregnation, the dried sample was subjected to pyrolysis, a high-temperature thermal degradation without oxygen. During pyrolysis, the impregnated SBP undergoes chemical reactions that convert organic molecules to carbonaceous material (Yang et al., 2019). After pyrolysis, the dark brown colour of the impregnated SBP changes to black, indicating that activated carbon was successfully prepared (Gan, 2021). The prepared SBMAC was washed with 0.1 M HCl and deionised water to remove impurities and neutralise the pH level of the SBMAC at 7~8. Impurities were successfully eliminated, as shown in Figure 4.5, where the colour of SBMAC turns to a darker shade of black.

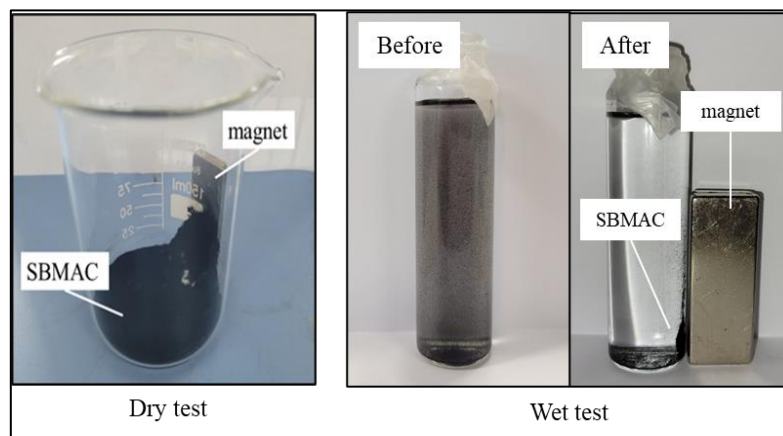


Figure 4.6: Response of SBMAC towards external magnet

On the other hand, the success of magnetic materials ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) impregnation onto SBMAC was verified by applying an external magnetic field to SBMAC. As shown in Figure 4.6, the verification was tested under two conditions, dry and wet. A magnet was placed at the side of a beaker containing a dry SBMAC for the dry test. Meanwhile, a wet test was done by vigorously mixing distilled water with SBMAC inside a glass tube and applying a magnet at the side of the tube. Based on both images, SBMAC was seen to be attracted to the external magnetic field applied during both tests. Thus, concluded that the magnetic materials were successfully impregnated onto SBMAC based on the response of SBMAC towards the magnetic field.

In conclusion, activated carbon with magnetic capabilities (SBMAC) was successfully prepared using the method provided in Section 3.4 and by implementing the optimal preparation parameters obtained in Section 4.1.3. The incorporation of magnetic materials into activated carbon can significantly improve the efficiency of activated carbon as an adsorbent, where the separation process of activated carbon from the system can be done by introducing a simple magnetic field.

4.3 Adsorbent Characterisation

4.3.1 BET Analysis

Table 4.8: The BET surface area and total pore volume of SBP, SBMAC, and SBMAC2

Adsorbent	Surface area (m ² /g)	Total pore volume (cm ³ /g)
SBP	25.382	0.125
SBMAC	849.906	2.470
SBMAC2	2.257	0.157

The Brunauer-Emmet-Teller (BET) method was utilised to determine the specific surface area and total pore volume of SBP, SBMAC, and SBMAC2, as shown in Table 4.8. Based on the tabulated data in Table 4.8, the specific surface area of SBP used as a precursor of SBMAC was measured at 25.382 m²/g, and the total pore volume was calculated to be 0.1249 cm³/g. Following the activation process, SBMAC showed a substantial increase in surface area to 849.906 m²/g and total pore volume to 2.470 cm³/g. This significant increase in surface area and total pore volume was attributed to the activation process, where the chemical activating agent (KOH) penetrated the carbon structure, resulting in the formation of microscopic pores in the SBMAC (Heidarinejad et al., 2020). Furthermore, after being utilised for the adsorption of methylene blue dye, the surface area and the total pore volume of SBMAC2 were determined at 2.257 m²/g and 0.157 cm³/g, respectively. The observed decrease in surface area and total pore volume after adsorption can be due to methylene blue ions occupying pores and active sites on the surface of the SBMAC. This result explains the high adsorption capacity of SBMAC, as the readily available sites were effectively used to accumulate and retain the methylene blue molecules. The characterisation of SBP, SBMAC, and SBMAC2 using BET

demonstrates the effect of the activation process and methylene blue adsorption on the surface properties of SBMAC.

4.3.2 FTIR Analysis

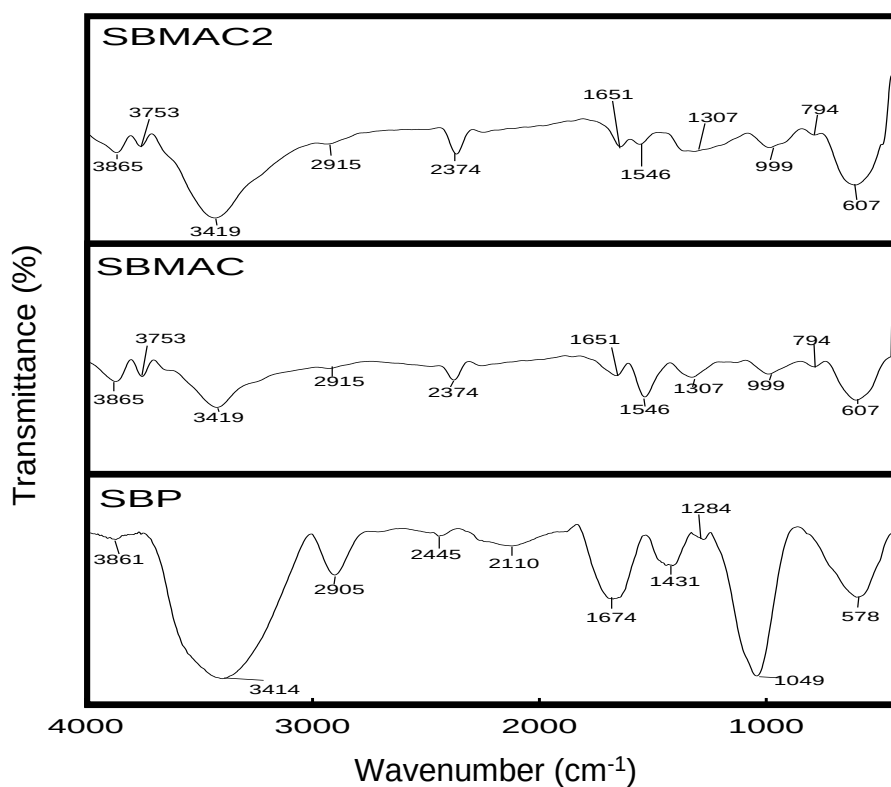


Figure 4.7: FTIR spectra of SBMAC2, SBMAC, and SBP

Fourier transform infrared (FTIR) spectroscopy was utilised to analyse the functional groups present in sago bark powder (SBP) and magnetic activated carbon derived from sago bark powder (SBMAC) and SBMAC after methylene blue adsorption (SBMAC2). FTIR spectroscopy is a powerful technique for identifying and characterising organic and inorganic compounds based on the absorption and transmission of infrared radiation. In this study, FTIR spectra of SBP, SBMAC and SBMAC2, as shown in Figure 4.7, were analysed by identifying the peaks that can be assigned to specific functional groups.

In SBP, a broad peak at 578 cm^{-1} can be attributed to the bending vibration of oxides on the surface of sago bark (Hegde et al., 2015), while the peak at 1049 cm^{-1} indicates the presence of alcohol, carbonyl, ester, and ether on the surface of SBP via C-O stretching vibrations (Abdullah et al., 2020). The peak at 1284 cm^{-1} is assigned to the C-O-C bending of ester, while the peak at 1431 cm^{-1} is due to COO- vibration, which is found in carboxylate polysaccharides and the side chains of amino acids (Kamnev et al., 2023). The peak at 1674 cm^{-1} indicates C=O stretching vibrations of ketones (Abdullah et al., 2020). The peaks at 2110 cm^{-1} and 2445 cm^{-1} are attributed to the presence of functional groups of nitriles (Shahin et al., 2022) and CO₂ (Parihar et al., 2019), respectively. The peak at 2905 cm^{-1} is attributed to the C-H stretching of the aliphatic group. Likewise, peaks at 3414 cm^{-1} and 3861 cm^{-1} indicate the presence of a hydroxyl group (Abdullah et al., 2020).

After the activation process, SBMAC showed weaker intensities of the peak of the functional groups compared to SBP. The peak at 607 cm^{-1} is attributed to Fe-O stretching vibration from iron oxide nanoparticles added during the impregnation process (Dirgayanti et al., 2021). In addition, several peaks in the SBMAC spectrum indicated the presence of various functional groups, including the peak at 1546 cm^{-1} is indicative of the presence of C=O stretching vibration of ketones and carbonyl (Yang et al., 2016), 1651 cm^{-1} may correspond to the C=O stretching band of carbonyl, carboxyl, and aromatic overtones (Geczo et al., 2021), and 999 cm^{-1} indicates the presence of C-O stretching vibrations (Fito et al., 2023). The diminished peak at 794 cm^{-1} and 2915 cm^{-1} indicates the presence of C-H band (Anyika et al., 2017; Huang et al., 2020). The peak at 1307 cm^{-1} and 2374 cm^{-1} are indicative of the presence of the C≡N group in the sample (Haider et al., 2021; Nail & Mendel, 2021), while the peak at 3419 cm^{-1} , 3753 cm^{-1} and 3865 cm^{-1} corresponds to O-H stretching vibrations in the hydroxyl group (Abdullah et al., 2020; Opoku et al., 2021).

After the methylene blue adsorption, the spectrum exhibits a notable increase in peak intensities but no apparent shift in peak locations, which is consistent with previous studies by Ebadollahzadeh and Zabihi (2020), and Kusuma et al. (2023) that found that peak locations were preserved despite only an increase in peak intensities. These showed that mechanical entrapment actively contributed to the methylene blue adsorption process (Kusuma et al., 2023). The change of peak intensities can be observed at peaks 3419 cm^{-1} , 2374 cm^{-1} , 1307 cm^{-1} and 607 cm^{-1} . The most apparent shift at peak 3419 cm^{-1} corresponds to the stretching vibration of O-H, which suggests that the positively charged methylene blue dye attracted the negatively charged O-H. Furthermore, the increase at peak 607 cm^{-1} intensities indicates the presence of C-Cl in methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$).

The functional groups in SBMAC indicate the successful synthesis of magnetic activated carbon from sago bark powder. The presence of peaks related to Fe-O stretching in SBMAC shows the successful incorporation of magnetic components into the activated carbon structure. Also, the presence of C-H bending in SBMAC2 after the adsorption indicates the presence of methylene blue on the surface of SBMAC2. Overall, the FTIR spectra of SBP, SBMAC and SBMAC2 provide valuable information about the chemical composition and functional groups present in these materials. These results can be useful for understanding the properties and potential applications of sago bark powder and magnetic activated carbon in various fields, such as water treatment. Table 4.9 shows the summary of the FTIR analysis of SBP, SBMAC and SBMAC2.

Table 4.9: FTIR analysis of SBP, SBMAC and SBMAC2

Sample	Wavenumber (cm ⁻¹)	Functional group
SBP	578	oxides
	1049	C-O
	1284	C-O-C
	1431	COO-
	1674	C=O
	2110	C≡N
	2445	CO ₂
	2905	C-H
	3414, 3861	-OH
SBMAC	607	Fe-O
	794,2915	C-H
	999	C-O
	1307, 2374	C≡N
	1546,1651	C=O
	3419, 3753, 3865	-OH
SBMAC2	607	Fe-O and C-Cl
	794,2915	C-H
	999	C-O
	1307, 2374	C≡N
	1546,1651	C=O
	3419, 3753, 3865	-OH

4.3.3 SEM-EDX Analysis

SEM analysis of SBP, SBMAC, and SBMAC2 was done to study the surface morphology of the adsorbents at different conditions, as shown in Figure 4.8. The SEM photograph of SBP shows a diverse surface roughness with numerous discernible pores, indicating that SBP has excellent potential as an adsorbent. In contrast, SBMAC has a more granular surface texture, exterior forms similar to SBP, and pores that appear partially blocked by a shining element, which is likely iron. On the other hand, the SEM image of SBMAC2 appears to be smooth compared to SBP and SBMAC granular texture. Also, the pores on the surface of SBMAC2 are less visible than in SBP and SBMAC images and more dull than in SBMAC. These observations suggest that the methylene blue ion has been adsorbed on the surface of SBMAC.

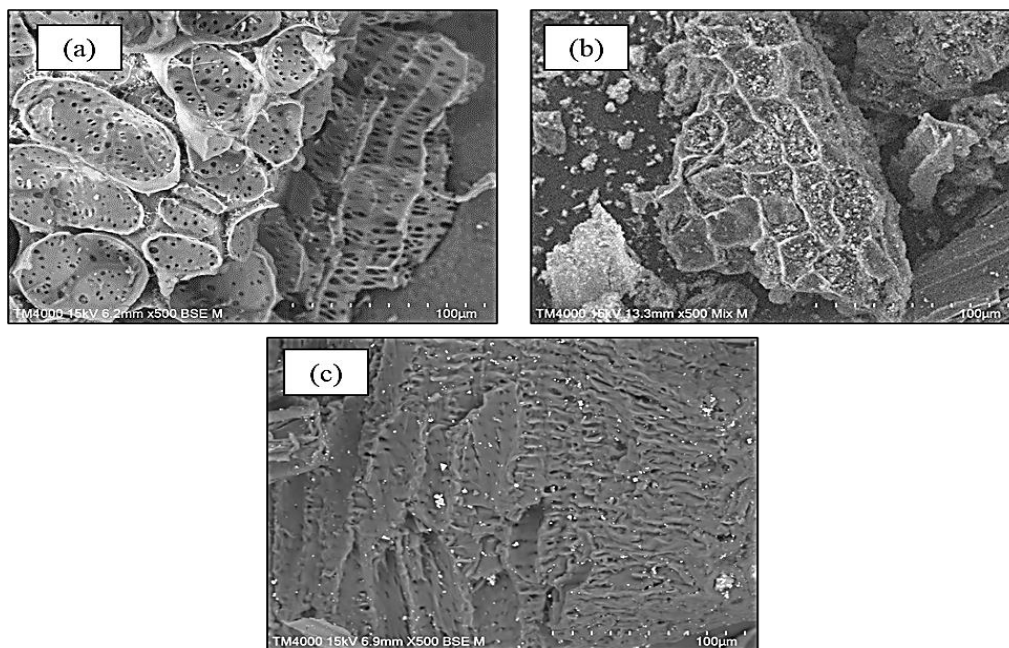


Figure 4.8: SEM images of (a) SBP, (b) SBMAC, and (c) SBMAC after adsorption at x500 magnification

EDX analysis was simultaneously done with SEM analysis to study SBP, SBMAC, and SBMAC2 surface elemental composition, and the results are shown in Table 4.10. As depicted in Figure 4.9, the number of elements for SBP, SBMAC, and SBMAC2 increases from 3 to 4 elements present on the adsorbents' surface. For SBP, 53.21% of carbon (C), 43.94% of oxygen (O), and 2.85% of aluminium (Al) elements were found. The presence of the Al element on the surface of SBP may be due to the physical pre-treatment process of SBP, which involved using aluminium foil to cover the adsorbent inside the drying oven. As for SBMAC, 81.41% of C, 9.61% of O, 0.39% of Al, 7.09% of iron (Fe), and 1.49% of nitrogen (N) were found. The mass percent of elements found on the surface of SBMAC2 is 72.44% of C, 13.36% of O, 3.68% of Al, 5.59% of Fe, 3.89% of N and 1.03% of Cl. Based on the SBMAC composition, the shining element observed in the SBMAC SEM image can be justified as Fe, which is not present on the surface of SBP. Also, the processing stages involved in SBMAC synthesis, particularly the pyrolysis under nitrogen flow and iron impregnation, may be responsible for the lower oxygen concentration

observed in SBMAC compared to SBP and the presence of N element. Meanwhile, SBMAC2, chlorine (Cl) was found on the surface of SBMAC2, which may be due to a reaction occurring during the adsorption of methylene blue molecules on the surface of SBMAC. Also, it was anticipated that the oxygen percentage would decrease due to the successful adsorption of methylene blue as the reaction between -OH and cationic dye took place. However, the oxygen percentage after adsorption increases based on the EDX analysis of SBMAC and SBMAC 2. This might be due to EDX analysis's difficulty in quantifying the precise percentages of elements, particularly oxygen, as EDX analysis focuses more on identifying the presence of different elements and their spatial distribution and has limited sensitivity to light elements such as oxygen (Konopka, 2012). The characterisation of SBP, SBMAC, and SBMAC provides insights into developing sustainable and eco-friendly materials from natural resources like sago bark.

Table 4.10: Elemental compositions of SBP, SBMAC, and SBMAC2

Elements	SBP	SBMAC	SBMAC2
	Mass percent (%)		
C	53.21	81.41	72.44
O	43.94	9.61	13.36
Al	2.85	0.39	3.68
Fe	-	7.09	5.59
N	-	1.49	3.89
Cl	-	-	1.03

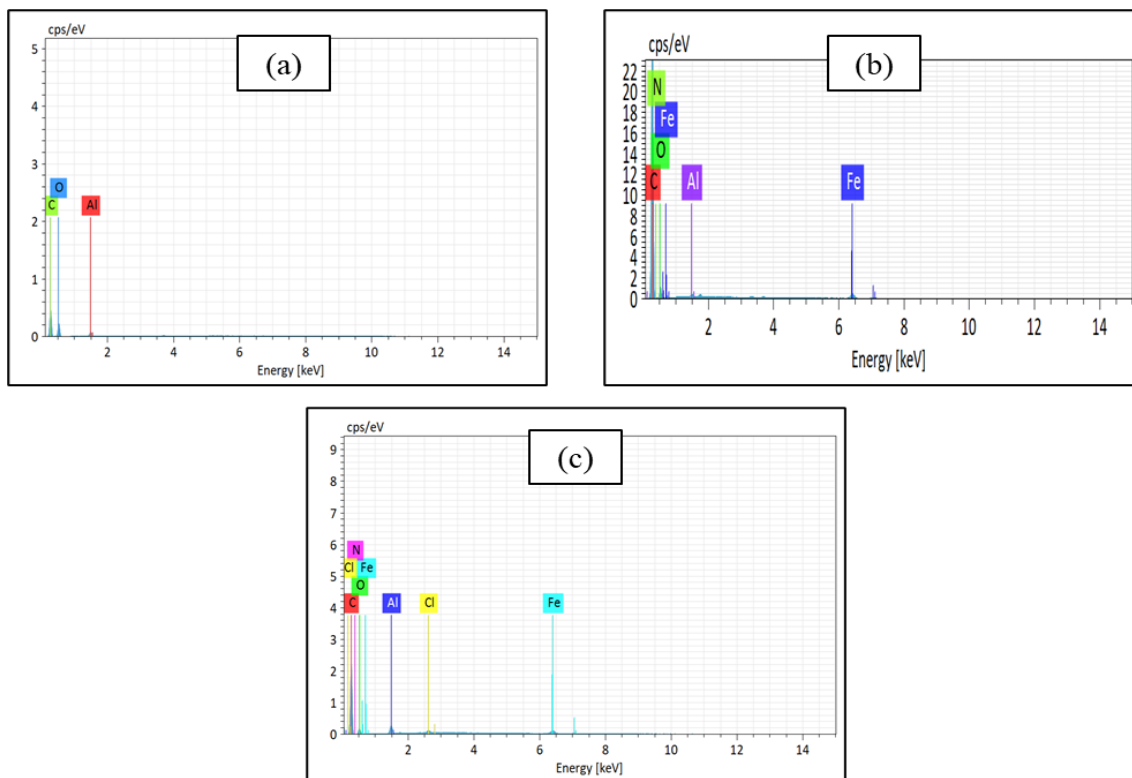


Figure 4.9: EDX analysis of (a) SBP, (b) SBMAC, and (c) SBMAC2

4.4 Adsorption Experiments

4.4.1 Kinetic Study

4.4.1.1 Batch kinetics at different initial concentrations of dye

The batch kinetics of methylene blue adsorption by using SBMAC at different initial concentrations of methylene blue were studied by varying the initial adsorbate concentration with a control volume of adsorbate at 100 mL and SBMAC dosage at 0.1 g/L for 24 hours. A total of 4 different initial concentrations of methylene blue 100, 200, 300 and 500 mg/L were stirred with 0.1 g/L of SBMAC at 150 rpm at constant temperature and pH of 30°C and pH 6, respectively. The effect of contact time on the adsorption capacity of SBMAC at different initial concentrations of methylene blue is shown in Figure 4.10.

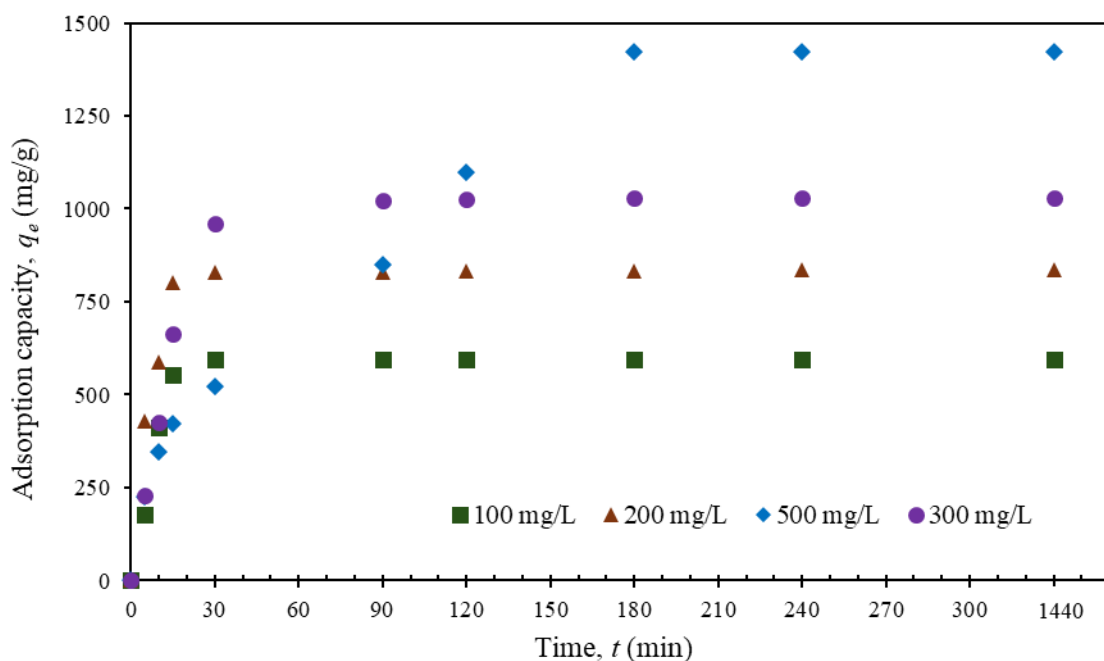


Figure 4.10: Effect of contact time on the adsorption capacity of SBMAC at different initial concentrations of methylene blue

Figure 4.10 shows that the adsorption capacity initially increases rapidly from 0 to 552.82 mg/g and 802.53 mg/g for initial concentrations of 100 mg/L and 200 mg/L, respectively, within the first 15 minutes. After reaching equilibrium at 30 minutes, the

adsorption capacity maintains at 594.18 mg/g and 834.34 mg/g for the same initial concentrations. Notably, the adsorption capacity increases by less than 50 mg/g within the 15 minutes from minute 15 to 30, indicating a significantly lower rate of adsorption compared to the first 15 minutes. This condition occurred due to the abundance of active sites available on SBMAC during the first 15 minutes of adsorption; thus, a large amount of methylene blue can be adsorbed faster. After 15 minutes of adsorption, the active sites began to be saturated, and methylene blue ions began to diffuse into the pores of SBMAC at a slower rate until they reached equilibrium.

For the higher initial concentrations of methylene blue at 300 mg/L and 500 mg/L, the rate of adsorption capacity increase is slower compared to the more diluted initial concentrations. In the first 15 minutes, the adsorption capacity increases from 0 to 664.13 mg/g and 423.69 mg/g, respectively. Both higher initial concentrations reach equilibrium at a slower rate, taking 90 minutes for 300 mg/L and 180 minutes for 500 mg/L. However, the adsorption capacities at equilibrium for 300 mg/L and 500 mg/L are higher compared to those for 100 mg/L and 200 mg/L.

According to Yao et al. (2020), the high adsorption rate at lower concentrations was due to a large number of active sites practicable for adsorption. In contrast, a slow adsorption rate reaches equilibrium at higher concentrations since more adsorption sites are occupied. This validates the experiment's findings that more diluted methylene blue takes less time to reach equilibrium than more concentrated methylene blue due to less competition between methylene blue ions, which increases the rate of ions adsorption on the surface of SBMAC.

Additionally, SBMAC adsorbed 594.18 mg/g, 834.34 mg/g, 1029.96 mg/g, and 1423.48 mg/g of methylene blue at equilibrium for initial methylene blue concentrations of

100 mg/L, 200 mg/L, 300 mg/L, and 500 mg/L, respectively. The corresponding adsorption efficiencies at equilibrium showed a decreasing trend, 59.4% at 100 mg/L, 41.72% at 200 mg/L, 34.33% at 300 mg/L and 28.5% at 500 mg/L. This decreasing adsorption efficiency trend can be attributed to the dye molecules competing for the limited number of active sites on the SBMAC as the initial concentration increases (Dimbo et al., 2024). On the other hand, the increase in adsorption capacity with a high initial concentration of methylene blue signifies more methylene blue ions in contact with the active sites of the adsorbent, which increases the diffusion of ions from the solution to the solid surface of SBMAC (Kuang et al., 2020). Based on these results, increasing the initial concentration of methylene blue increases SBMAC's adsorption capacity at equilibrium, and decreases the adsorption efficiency of SBMAC. Thus, a larger gradient between the initial concentration of adsorbate and adsorbent dosage may increase the adsorption capacity but lower the adsorption efficiency.

4.4.1.2 Kinetic modelling

Adsorption kinetic was studied using three adsorption kinetic models, pseudo-first-order (PFO), pseudo-second-order (PSO), and intra-particle diffusion Weber-Morris (ID) model which provides the adsorption rate, performances of SBMAC and the mass transfer involved. A kinetic study was done at four different initial concentrations of 100, 200, 300 and 500 mg/L. Other adsorption parameters were kept constant ($T = 303$ K, dosage of SBMAC = 0.1 g/L, time = 1440 min, and pH = 6). All calculated kinetic parameters were tabulated in Table 4.11.

Table 4.11: Parameters of adsorption kinetic model

Kinetic models		Methylene blue concentration			
		100 mg/L	200 mg/L	300 mg/L	500 mg/L
Experimental	q_e (mg/g)	594.1766	834.3369	1029.9613	1423.4822
Pseudo-first-order (PFO)	q_e (mg/g)	601.4029	837.3109	1035.8379	1433.3178
	k_1 (min ⁻¹)	0.1106	0.1428	0.0634	0.0141
	R^2	0.9727	0.9906	0.9901	0.9569
	SSE	1.12×10^4	6.45×10^3	1.70×10^3	1.14×10^5
Pseudo-second-order (PSO)	q_e (mg/g)	595.4225	835.3441	1035.1313	1456.2524
	k_2 (g/mg·min)	7.46×10^{-4}	8.82×10^{-4}	1.76×10^{-4}	2.32×10^{-5}
	h (mg/g·min)	264.4669	615.2032	188.1386	49.2234
	R^2	0.9999	0.9999	0.9998	0.9977
	SSE	3.47×10^{-5}	3.78×10^{-5}	3.21×10^{-4}	1.88×10^{-3}

The best-fitting model between PFO and PSO was determined by two statistical parameters, correlation coefficient (R^2) and sum of squares error (SSE). A closer value of R^2 to 1.0 indicates that the model predicts the data better, while the smaller SSE value indicates a lower model deviation from the experimental data. According to table 4.11 data, the experimental data favours the PSO kinetic model, and the fit to this model yielded the highest correlation coefficient (R^2) of 0.9999, 0.9999, 0.9998, and 0.9977 for

adsorption at 100 mg/L, 200 mg/L, 300 mg/L, and 500 mg/L, respectively compared to the PFO kinetic models. Also, all SSE calculated for PSO kinetic models are lower than PFO kinetic models, indicating that PSO model have lower deviations from the experimental data. Therefore, PSO kinetic model is better suited for defining methylene blue adsorption onto SBMAC compared to PFO kinetic model. This is preferable because PFO primarily reflect the beginning of the adsorption, when the difference between the concentration of the methylene blue and the amount of adsorbed is the largest. PFO kinetic model assumes that the adsorption rate is linearly proportional to this difference (Sahoo & Prelot, 2020). As the adsorption progresses, the number of active sites decreases, and the rate of adsorption no longer follows a simple proportional relationship, making the model less accurate for the subsequent stages of adsorption.

In addition, the PSO kinetic model assumes that the adsorption process is primarily controlled by chemisorption, where chemical bonds form at active sites on the adsorbent (Sahoo & Prelot, 2020). This indicates that the adsorption rate is more influenced by the number and availability of these active sites than by the concentration of methylene blue in the solution (Wang & Guo, 2020). Since the PSO model fits the adsorption of methylene blue onto SBMAC better than the PFO model, it suggests that SBMAC has a large number of effective active sites, which are crucial for achieving high adsorption capacity. Furthermore, most previous research suggests that methylene blue adsorption employing magnetic activated carbon is best suited to the PSO kinetic model (Abuzerr et al., 2018; Ebadollahzadeh & Zabihi, 2020; Kittappa et al., 2020).

Based on table 4.11, there are three kinetic parameters determined from the PSO kinetic model, which are the equilibrium adsorption capacity (q_e), PSO rate constant (k_2), and initial sorption rate (h). The equilibrium adsorption capacity of methylene blue

calculated by the PSO kinetic model increased from 595.4225 to 1456.2524 mg/g as the initial concentration of methylene blue increase from 100 to 500 mg/L, which correlates with the experimental equilibrium adsorption capacity values. On the other hand, the equilibrium adsorption capacity derived using this PFO model has a wider gap from the experimental adsorption capacity because the regression coefficient is lower than in the PSO kinetic model. Meanwhile, the highest PSO rate constant (k_2) and initial sorption rate (h) were calculated for the adsorption of 200 mg/L initial concentration, followed by the adsorption of 100 mg/L, 300 mg/L, and 500 mg/L. The initial sorption rate of 100 mg/L, 200 mg/L and 300 mg/L were higher than 100 mg/g.min, while an initial sorption rate of 500 mg/L was calculated at 49.2234 mg/g.min indicates that the adsorption rate is initially faster at lower concentrations of methylene blue dye.

Table 4.12: Parameters of ID kinetic model

Parameters	Methylene blue concentration			
	100 mg/L	200 mg/L	300 mg/L	500 mg/L
k_{id} (mg/g.min ^{1/2})	10.061	12.835	21.835	38.933
c (mg/g)	367.47	552.73	518.50	376.22
R^2	0.2691	0.2505	0.3784	0.6254

In contrast to PFO and PSO kinetic models, the ID kinetic model predicts that methylene blue diffusion onto SBMAC pores is the slowest phase in the adsorption mass transfer and that methylene blue diffusion onto active sites is the fastest. Table 4.12 shows the calculated parameters of the ID kinetic model for different methylene blue concentrations (100, 200, 300, and 500 mg/L). The low correlation coefficients (R^2) for all concentrations indicate that the ID model does not fit the experimental data well. Specifically, the R^2 values are 0.2691 for 100 mg/L, 0.2505 for 200 mg/L, 0.3784 for 300 mg/L, and 0.6254 for 500 mg/L, suggesting a poor fit of the ID model. However, the ID

kinetic model can still provide valuable insights. The boundary thickness parameter (c) for all four concentrations is not zero, with values of 367.47 mg/g for 100 mg/L, 552.73 mg/g for 200 mg/L, 518.50 mg/g for 300 mg/L, and 376.22 mg/g for 500 mg/L. This implies that intra-particle diffusion is not the only process controlling the adsorption of methylene blue onto SBMAC. Instead, the adsorption process is influenced by multiple processes, as assumed by ID kinetic model (Wang & Guo, 2020). Furthermore, the rate constant for intra-particle diffusion (k_{id}) increases with the concentration of methylene blue, with values of 10.061 mg/g.min^{1/2} for 100 mg/L, 12.835 mg/g.min^{1/2} for 200 mg/L, 21.835 mg/g.min^{1/2} for 300 mg/L, and 38.933 mg/g.min^{1/2} for 500 mg/L. These findings highlight the complexity of the adsorption process, indicating that it cannot be adequately described by the ID kinetic model alone and suggesting the involvement of other concurrent processes.

4.4.2 Adsorption Isotherm

The adsorption isotherm of SBMAC was studied by determining the equilibrium concentration and adsorption capacity of methylene blue and SBMAC, respectively. The study was done by varying the initial concentration of methylene blue ranging from 80 to 500 mg/L for 24 hours. Other adsorption parameters were controlled (pH 6, T = 303 K and, stirring speed = 150 rpm). By using the data obtained, all data were analysed using Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm model. All calculated isotherm parameters were tabulated in Table 4.13.

Table 4.13: Parameter of adsorption isotherm model

Model	Adsorption parameters				
Langmuir	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	χ^2
	1655.05	0.0091	0.1807	0.9257	102.93
Freundlich	$1/n$	K_F (mg/g)·(mg/L) ^{1/n}		R^2	χ^2
	0.4103	115.3180		0.9662	31.10
Temkin	b	A_t (L/g)	B (J/mol)	R^2	χ^2
	7.3817	0.1069	293.51	0.9050	73.75
Dubinin-Radushkevich	q_m (mg/g)	E		R^2	χ^2
	1018.55	59.3937		0.7015	202.16

According to tabulated data in Table 4.13, the experimental data favours the Freundlich isotherm model, and the fit to this model yielded the highest regression (R^2) of 0.9662 and the lowest chi-square (χ^2) of 31.10 outperforming the Langmuir, Temkin and DR isotherm models. Studies by Alver et al. (2020), Azam et al. (2020), and Yağmur and Kaya (2021) also show that the adsorption of methylene blue solution using magnetic activated carbon was best fitted with the Freundlich isotherm model. Freundlich isotherm model assumes that the adsorption process is multilayers on heterogeneous surfaces and commonly used to describe activated carbon adsorption in an aqueous solution (Worch, 2021). Based on the assumptions of Freundlich isotherm, K_F and $1/n$ were determined at 115.3180 (mg/g)·(L /mg)^{1/n} and 0.4103, respectively. The value of K_F is considered high when compared to values studied from other magnetic-activated carbons (Alver et al., 2020; Azam et al., 2020; Chen et al., 2019; Mohammadi et al., 2020; Yağmur & Kaya, 2021), which is desirable because a high value of K_F indicates a higher loading of methylene blue onto SBMAC. $1/n$ is also Freundlich's parameter, which correlates to the energy heterogeneity of the SBMAC surface and the adsorbate loading favourability. The

value of $1/n$ calculated from the Freundlich isotherm model is in the range of 0 to 1, indicating that methylene blue adsorption onto SBMAC is favourable because the loading of methylene blue is high at a low concentration, resulting in more efficient adsorption.

Aside from the parameters of the Freundlich isotherm, the parameters of the Langmuir, Temkin, and DR isotherms can assist in comprehending the adsorption mechanism of SBMAC. Langmuir isotherm model suggests that methylene blue binds to the SBMAC surface through monolayer adsorption and the maximum monolayer adsorption capacity is determined at 1655.05 mg/g. This implied that 1.0 g of SBMAC could be adsorbed up to 1655.05 mg of methylene blue ions. SBMAC's q_{max} is compared with other studies done in the past for the removal of methylene blue using different types of magnetic-activated carbon as an adsorbent as shown in Table 4.14. As shown in Table 4.14, SBMAC has a relatively high maximum adsorption capacity when compared to other adsorbents that demonstrate its potential. A high adsorption capacity indicates that a small amount of adsorbent is required to fully adsorb a high concentration adsorbate which has shown a good prospect for SBMAC as an effective adsorbent. Aside from q_{max} , Langmuir constant, K_L and separation factor, R_L is also determined by the Langmuir model's linear regression. K_L was used to determine R_L , which came to the value of 0.1807. R_L is used as an indicator to predict adsorption desirability. Adsorption is considered favourable when the value of R_L falls between 0 and 1. Therefore, it can be stated that methylene blue adsorption by SBMAC is favourable as the value of R_L calculated is in the range of 0 to 1.

Table 4.14: The comparison of studies using magnetic activated carbon for methylene blue removal

Adsorbent	Maximum adsorption capacity, q_{max} (mg/g)	References
Magnesium and silica-coated magnetised palm shell-activated carbon	369.5	(Kittappa et al., 2020)
Magnetic alginate/rice husk bio-composite beads	344.0	(Alver et al., 2020)
Magnetic wakame biochar nanocomposites	552.5	(Yao et al., 2020)
Magnetic ball-milled activated carbon (hickory chip)	304.2	(Li et al., 2020)
Magnetic-activated carbon-cobalt nanoparticles (sea-buckthorn stone)	192.3	(Mohammadi et al., 2020)
Nano-magnetic activated carbon (peach stone and wood)	434.1	(Ebadollahzadeh & Zabihi, 2020)
Eucalyptus sawdust magnetic activated carbon	192.3	(Chen et al., 2019)
Magnetic ZnCl ₂ -activated carbon (coconut shell)	156.3	(Yağmur & Kaya, 2021)
SBMAC	1655.05	This study

Meanwhile, the Temkin isotherm model assumed that the heat adsorption of all molecules in the layer reduces linearly with increase surface coverage, and that indirect adsorbate-adsorbent relations have no effect on the adsorption process. From this model, b , A_T , and B were determined at 7.382, 0.1069 L/g, and 293.51 J/mol, respectively. b is the Temkin isotherm constant, B is the Temkin isotherm constant related to the heat of adsorption, whereas A_T is the Temkin isotherm equilibrium binding constant. Furthermore, another prevalent isotherm model used to study the adsorption mechanism is the DR isotherm model, which assumes multilayer adsorption with Van Der Waal's forces. q_m and E are calculated by using this isotherm model at 1018.545 mg/g and 59.394 kJ/mol, respectively. q_m is the maximum adsorption capacity of SBMAC, while E is the mean free

energy during the adsorption. Based on the calculated mean free energy, the adsorption process of methylene blue onto SBMAC is dominated by chemical adsorption as the value of mean free energy greater than 16 kJ/mol. A study by Chen et al. (2019) on the adsorption of methylene blue by Eucalyptus sawdust magnetic activated carbon yielded a mean free energy of 46.65 kJ/mol, which is also higher than 16 kJ/mol.

Figure 4.11 shows the relationship between the calculated isotherm models with the experimental data. The parameters for the nonlinear equation of the isotherm model were obtained from the linear equation plot of the isotherm model and thus allowed for the generation of the corresponding graph. Based on Figure 4.11, as the equilibrium concentration of methylene blue increases, the adsorption capacity of SBMAC also increases, which correlates with the study of the effect of initial concentration in Section 4.4.1.1. Furthermore, only the DR isotherm model deviates more from the experimental data than the other models. This can be explained by the fact that the DR isotherm model's regression coefficient was only 0.7015, while the regression coefficients of other isotherm models were more than 0.90. The substantial regression ($R^2 = 0.9662$) value of the Freundlich model suggested that this model can better explain the adsorption properties compared to the other isotherm model. Thus, the process of methylene blue adsorption onto SBMAC is heterogeneous adsorption following the Freundlich isotherm assumptions.

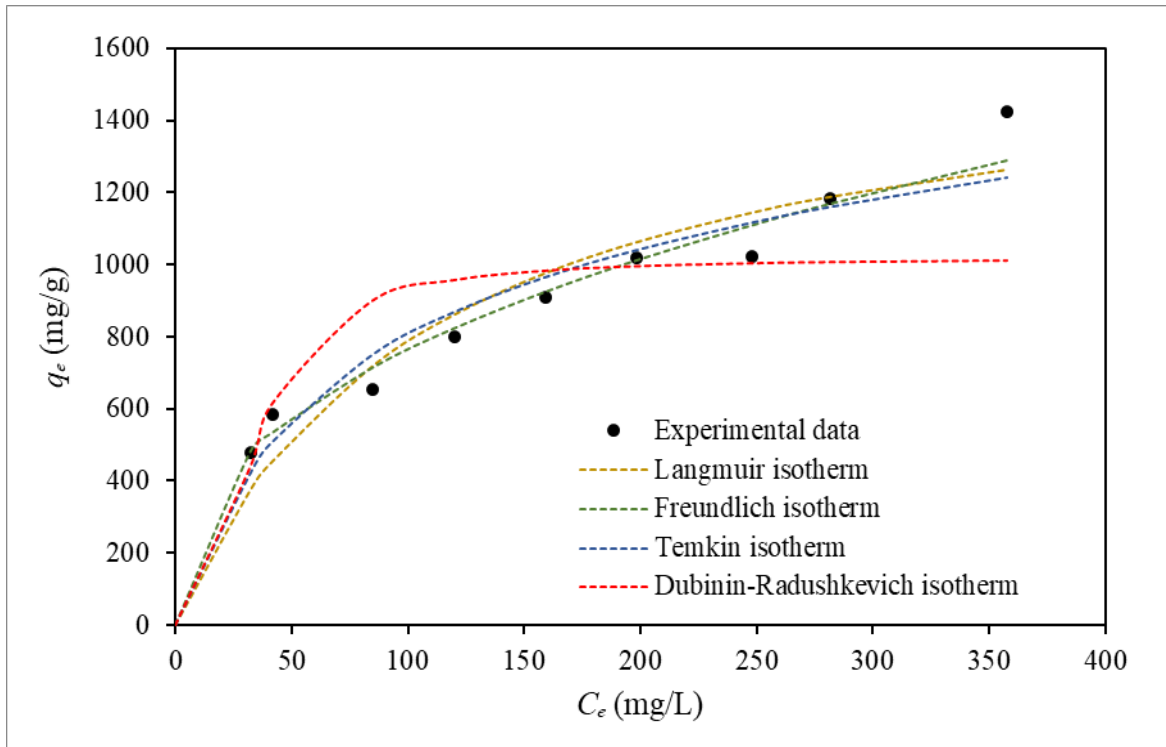


Figure 4.11: Comparison of experimental data with the adsorption isotherm models

4.4.3 Effect of Temperature and Adsorption Thermodynamics

The effect of temperature and thermodynamic parameters on methylene blue adsorption by SBMAC was studied at four different temperatures ranging from 303K to 333K. Other adsorption parameters were controlled (initial concentration of methylene blue = 100 mg/L, the dosage of SBMAC = 0.1 g/L, time = 90 min, and pH = 6). Following the experiment's outcomes, T=303 K had the highest adsorption capacity among the four temperatures studied at 686.91 mg/g. Meanwhile, at an adsorption temperature of 323K, the lowest adsorption capacity of 551.35 mg/g was observed. Also, when the temperature rises to 333K, the adsorption capacity of SBMAC rises to 575.56 mg/g. However, the adsorption capacity of SBMAC at 323K and 333K was still low when compared to temperatures set at 303K and 313K, which differed by more than 15%, as shown in Figure 4.12.

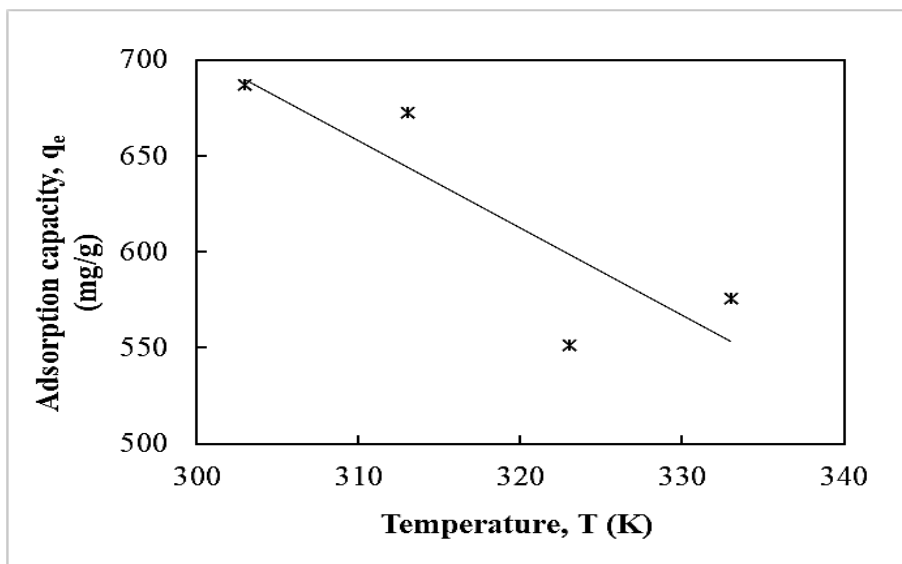


Figure 4.12: Effect of temperature on adsorption capacity of SBMAC

Thermodynamic parameters, namely change of Gibbs energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°), were investigated. All parameters were calculated using Equations

2.14 and 2.16. Graph of $1/T$ vs $\ln K_d$ is plotted as shown in Figure 4.13 to solve Equations 2.14 and 2.16. Based on the graph, ΔS° and ΔH° were determined by the slope and the y-intercept of the graph. All thermodynamic parameters data from the adsorption of methylene by SBMAC were tabulated in Table 4.15. As shown in Table 4.15, all thermodynamic parameter values calculated are less than zero. ΔG° at all measured temperatures less than zero indicates that the adsorption process of methylene blue by SBMAC is feasible and spontaneous.

Table 4.15: Thermodynamic parameters for removal of methylene blue by SBMAC

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol.K)
303	-7.7799	-16.4837	-28.567
313	-7.8630		
323	-6.7369		
333	-7.2180		

Additionally, since the value of change of Gibbs energy was determined to be in the range of -20 to 0 kJ/mol, physical adsorption is likely to be the adsorption mechanism. Meanwhile, the adsorption of methylene blue by the novel adsorbent was an exothermic process, as evidenced by the negative value of the change of enthalpy obtained in the experiment ($\Delta H^\circ = -16.4837$ kJ/mol) and also the decrease in adsorption capacity as the temperature rises. On the other hand, the negative value of change of entropy was also determined to be negative, indicating the decline in volatility at the solid-solution interface during the adsorption. The same outcomes were attained by (Ye et al., 2020) for the adsorption of methylene blue using a mesoporous magnetic silica composite, where all thermodynamic parameters calculated are negative.

Therefore, based on the effect of the temperature experiment, the best adsorption temperature is at the lowest temperature tested ($T=303K$), where the highest adsorption

capacity was recorded. This further reveals that the adsorption of methylene blue by SBMAC is exothermic. Furthermore, the calculated thermodynamic parameters show that using SBMAC as a methylene blue adsorbent is feasible, and the solid-solution interface is more predictable.

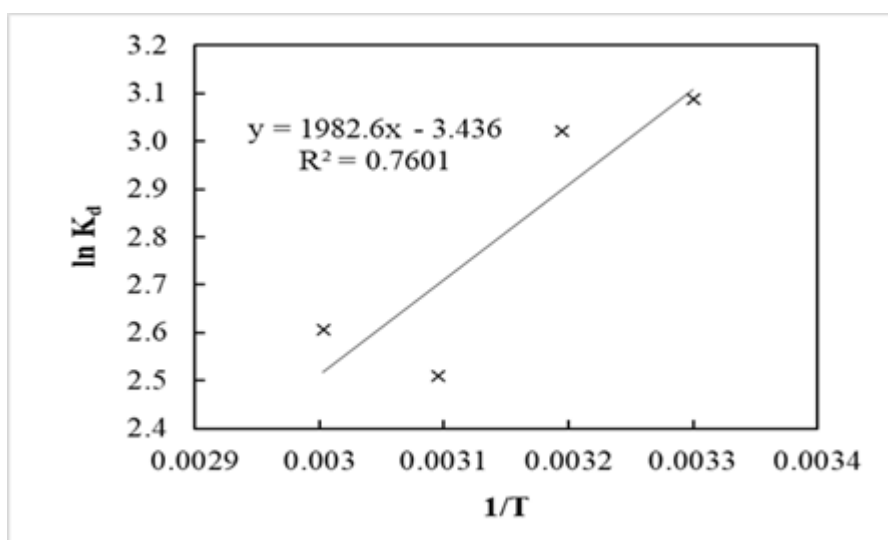


Figure 4.13: Plot of $\ln K_d$ vs $1/T$ for methylene blue adsorption by SBMAC

4.4.4 Effect of Adsorbent Dosage

The mass of SBMAC was varied to study the effect of SBMAC dosage on the adsorption of methylene blue with a control volume of adsorbate at 50 mL. A total of 5 different masses of SBMAC ranging from 0.005 g to 0.1 g were introduced to 50 mL of 50 mg/L methylene blue solution and stirred at 150 rpm for 90 mins at a constant temperature of 30°C and pH 6. The final concentration of methylene blue and the removal efficiency of SBMAC were determined. The relation of SBMAC dosage with methylene blue removal efficiency was plotted in Figure 4.14.

Based on Figure 4.14, when the adsorbent dosage was increased from 0.05 to 2.0 g/L, the adsorption percentage increased and remained constant once it achieved 100%

removal. 100% methylene blue removal was achieved when the SBMAC dosage was more than 0.05 g/L since more SBMAC active sites were present per unit volume of solution. A higher dosage of adsorbent results in better adsorption efficiency as the greater surface area can be associated with methylene blue molecules (Lawagon & Amon, 2020).

Consequently, as SBMAC dosage increased, the percentage of methylene blue removal increased significantly, but the increase of adsorbent dosage is insignificant after 1.0 g/L as the adsorption efficiency had already reached its maximum at a lower dosage. Hence, the SBMAC dosage of 1.0 g/L was chosen as the optimal dose for removing methylene blue.

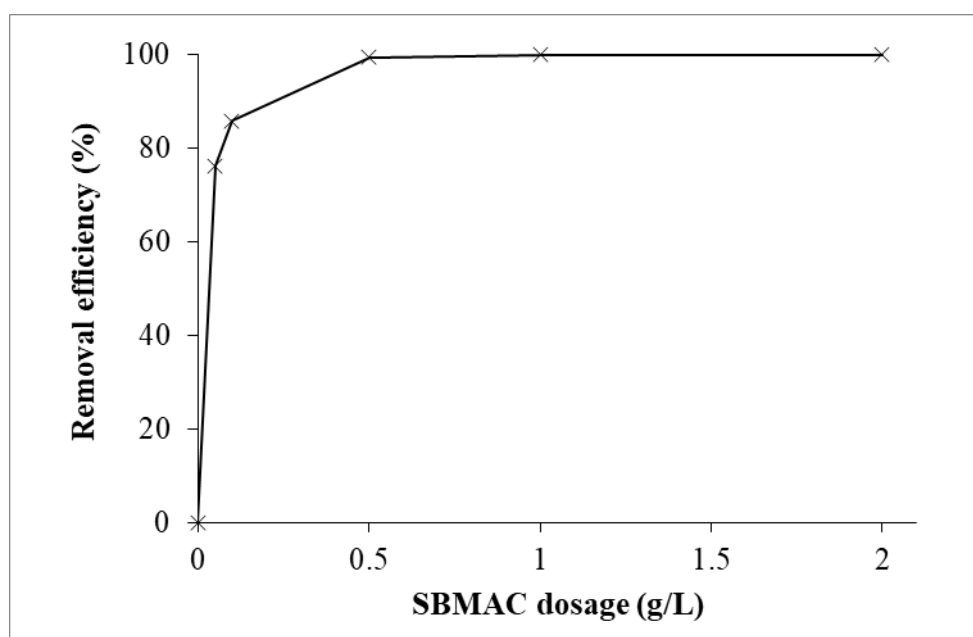


Figure 4.14: Effect of SBMAC dosage on removal efficiency

4.4.5 pH of the Point of Zero Charge (pH_{PZC}) of SBMAC and the Effect of pH

The pH_{PZC} of SBMAC and the effect of adsorbate pH were studied as both are the most crucial adsorption parameters for optimising an adsorbent's performance, as they influence the ion exchange and electrostatic interactions during adsorption. The point of zero charges (pH_{PZC}) was obtained by plotting the final pH graph and the initial pH graph, as shown in Figure 4.15. Based on the plot, pH_{PZC} was determined at pH 6.74. pH_{PZC} is regarded as a significant adsorbent feature as no electrostatic interactions happen between SBMAC active sites and methylene blue dye ions at this pH, which substantially affects the adsorption. Moreover, the adsorption capacity of SBMAC dropped when the initial pH was lower than pH_{PZC} and rose when the initial pH was higher than pH_{PZC} (Jiaqi et al., 2019).

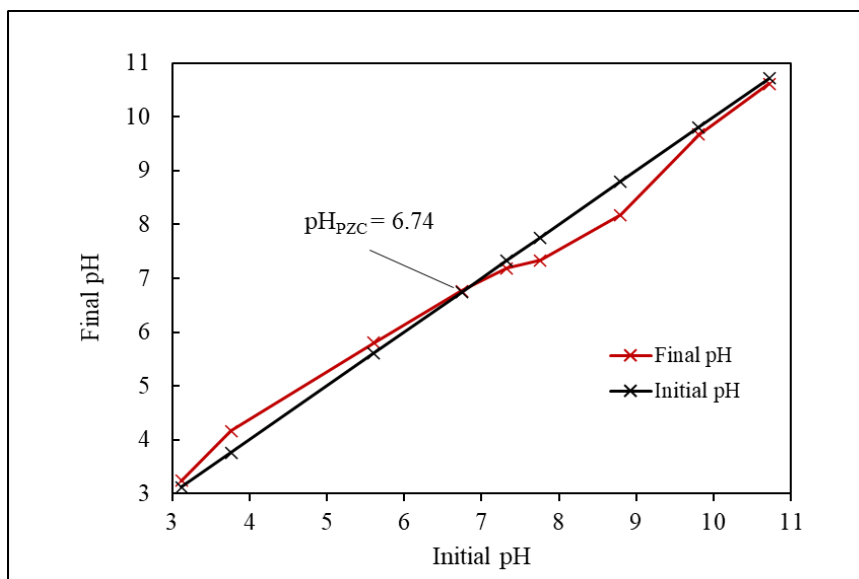


Figure 4.15: pH of point of zero charge (pH_{PZC}) of SBMAC

The effect of pH of methylene blue was studied by varying its pH between 3 and 11. Nine 150 mL Erlenmeyer flasks were filled with 50 mL of methylene blue and shaken with 5 mg of SBMAC at 150 rpm and 30°C until equilibrium was reached. The equilibrium concentration and pH of methylene blue were measured. The adsorption capacity of methylene blue solution at pH 7 is 529.106 mg/g. The highest recorded adsorption capacity of SBMAC is 598.459 mg/g at pH 11, while the lowest recorded adsorption capacity is 254.136 mg/g at pH 3.

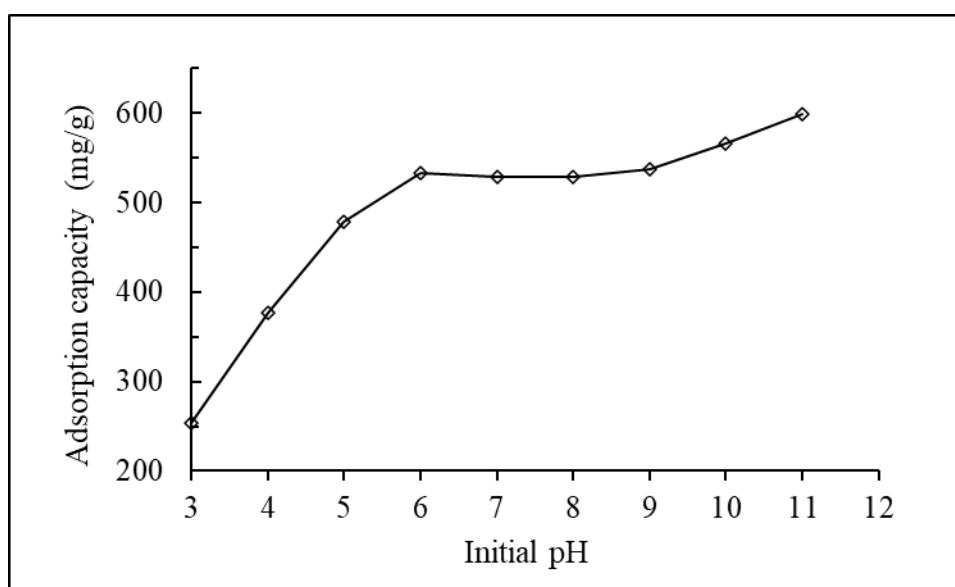


Figure 4.16: Effect of pH on adsorption capacity

Based on Figure 4.16, as the initial pH of methylene blue increases, the amount of methylene blue molecules adsorbed on the surface of SBMAC also increases. A slight increase in adsorption capacity was recorded at pH 6 to 8, while the sample exhibits a rapid increase in absorption value above pH 9 when pH shifts from 9 to 11. High adsorption capacity at higher pH is attributed to less competition between positive charge methylene blue ions and H_3O^+ ions to be adsorbed on the surface of SBMAC, as well as the lower volume of proton that protonates with the negatively charged adsorbent (Singh et al., 2021).

The adsorption capacity of SBMAC was found to be the lowest at the most acidic state of methylene blue solution and the highest at the highest alkalinity of methylene blue solution which validated the value of pH_{PZC} . Thus, the initial pH of cationic methylene blue and pH_{PZC} of SBMAC significantly influenced the adsorbent's adsorption capacity and would be enhanced under more basic conditions.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In conclusion, SBMAC was successfully synthesised by employing the most optimal preparation parameters via single-stage pyrolysis, with the successful incorporation of Fe^{2+} and Fe^{3+} using the impregnation method. Also, SBMAC was effectively activated using KOH as the activating agent. Based on the optimisation study of SBMAC preparation parameters, the most optimal impregnation ratio, pyrolysis temperature, and heating time are proposed at 1.5, 700°C, and 60 minutes, respectively.

SBMAC was characterised and compared to SBP and SBMAC2 using BET, FTIR, and SEM-EDX analysis. Based on the BET analysis, SBMAC shows the highest specific surface area and total pore volume compared to SBP and SBMAC2 at 849.906 m^2/g and 2.47 cm^3/g , respectively. The increase in surface area and total pore volume of SBMAC from SBP shows that the activation process was successful. Also, the decrease of surface area and total pore volume after the adsorption shows that methylene blue ion successfully adsorbed on the surface of SBMAC. On the other hand, FTIR analysis of SBMAC shows the presence of Fe-O functional group at 607 cm^{-1} , which is not present during SBP analysis, indicating the successful incorporation of magnetic components into the activated carbon structures. Also, the significant shift at peak intensities at 3419 cm^{-1} and 607 cm^{-1} after the adsorption of methylene blue suggest the electrostatic attraction between -OH band and the presence of C-Cl band, respectively. Consistent location of peaks after the adsorption suggests that mechanical entrapment is one of the adsorption mechanisms.

Furthermore, SEM images show SBP has discernible pores compared to SBMAC, where shining elements partially block pores. Also, SBMAC2's SEM image is smoother, and pores are less visible. As for the EDX analysis, a high percentage of C and O elements was observed for SBP, and a high percentage of C, O, and Fe was observed on the surface of SBMAC and SBMAC2, proving the successful incorporation of iron elements into the activated carbon. Also, Cl was present on SBMAC2 may be due to the adsorption of methylene blue dye.

The adsorption behaviours were analysed based on the study of kinetic, isotherm, the effect of temperature and thermodynamics, effect adsorption dosage, and the effect of pH and pH_{PZC} . Based on the study, the kinetics shows that the increase in initial dye concentration decreases the adsorption rate, with the estimated equilibrium time of adsorption at 30 minute, 90 minute and 180 minute for 100-200 mg/L, 300 mg/L, and 500 mg/L, respectively. On the other hand, the best-fitted kinetic model is the PSO model instead of the PFO model, which implies that SBMAC contains a high number of active sites. Also, the kinetic data does not fit the ID model, suggesting that adsorption is not solely controlled by intra-particle diffusion. As for the isotherm study, the adsorption capacity is directly proportional to the initial concentration of methylene blue dye, and the best-fitted isotherm model is the Freundlich isotherm model, which implies that the adsorption is heterogeneous with maximum adsorption capacity evaluated at 1655.05 mg/g.

Furthermore, the study on the effect of temperature shows that the highest adsorption capacity was obtained at 30°C, and the adsorption process was exothermic. Also, based on the calculated thermodynamic parameters, the adsorption of methylene blue dye using SBMAC is feasible, and the solid-solution interface is predictable. The study of

adsorbent dosage shows as SBMAC dosage increased, the adsorption efficiency of SBMAC increased. However, the increase of adsorbent dosage to a certain amount became insignificant as the efficiency reached 100% at lower dosages. Thus, the most optimal dosage of SBMAC was obtained at 1.0 g/L. Additionally, the pH_{PZC} obtained was at pH 6.74, suggesting that no electrostatic interactions occur at this pH. The study of the effect of pH shows the increased trend of adsorption capacity with the increase of pH, which shows the adsorption process of methylene blue was ideal under basic conditions of pH 11. The electrostatic attraction between the cationic methylene blue and the negatively charged surface of activated carbon is typically stronger at pH values above the pH_{PZC} .

5.2 Recommendations

Based on the outcomes of this research, multiple further studies can be conducted to further assess and improve the practicability of SBMAC as an adsorbent. The future studies that can be conducted include the comparative analysis of SBMAC preparation methods, the comprehensive characterisation of SBMAC, the SBMAC versatility in pollutant removal, and the systematic optimisation of SBMAC preparation parameters.

In order to further refine the SBMAC preparation process, it is suggested to add more process variables for the optimisation study. This includes the effect of nitrogen gas flowrate, impregnation ratio of activating agent, and SBMAC particle sizes. This will provide valuable insights into the influence of these parameters on SBMAC's properties, assisting a more controlled and effective production process.

In order to acquire a better understanding of SBMAC synthesis, it is recommended that SBMAC be prepared using different methods, such as microwave-assisted pyrolysis and co-precipitation method. This comparison analysis aims to provide valuable insights into the performance of each method in terms of magnetic characteristics, surface area, and

capacity for pollutant adsorption. Through the process of evaluating and contrasting various strategies, it is possible to attain an in-depth understanding of the advantages and drawbacks.

In addition, SBMAC should be analysed with more analysis methods rather than three to provide a more thorough understanding of SBMAC characteristics. Examples of analysis that can be added are X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), and a magnetometer. This analysis will provide a better understanding of SBMAC's physical and chemical characteristics such as crystal structures, thermal stability, and magnetic attributes.

Moreover, in order to fully assess the capabilities of SBMAC as an adsorbent, it is recommended to study the efficacy of SBMAC in removing other types of wastewater contaminants such as heavy metals, dissolved inorganics, and organic matter. The experimental analyses can be performed to determine the adaptability and potential applications of SBMAC's adsorption capacity and kinetics for these pollutants.

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